

A TEXT BOOK OF METALLOGRAPHY

CHEMISTRY AND PHYSICS OF THE
METALS AND THEIR ALLOYS

BY

GUSTAV TAMMANN

Director, The Institute for Physical Chemistry in Göttingen

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WITH THE PERMISSION OF THE AUTHOR

BY

REGINALD SCOTT DEAN *and* LESLIE GERALD SWENSON

Metallurgical Engineers, Western Electric Company, Inc.

BOOK DEPARTMENT

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I. ONE COMPONENT SYSTEMS

A. The Process of Crystallization

1. The Genesis of the Structure of a Metal.

The pure cast metals are revealed by microscopic investigation as conglomerates of closely packed polyhedra of about 0.1 to 0.01 mm. diameter. These polyhedra frequently have a granular shape while less frequently, they are prismatic, e.g. Zn, Sb and Bi.

If the polished section of a piece of metal crystallized from the melt is etched with appropriate etching agents, we find that the etching has brought out a polygonal pattern on the section by means of almost straight lines which form a network (Fig. 1). The fine lines represent the intersections of the polyhedral boundary surfaces with the plane of the section.

The formation of the polyhedra takes place during crystallization in the following way. On cooling a melt, crystal centers (nuclei) are formed and from these the crystals grow either as spherulites or crystal polyhedra. In both cases the crystals grow together so that the boundary planes which are formed are not regularly oriented with respect to the axes of the elementary crystals. The boundary planes of the grains, of which a metal crystallized from a melt is built up, are accordingly not to be confused with crystal planes. Such forms are accordingly designated not as crystals but as crystallites, without forgetting that the substance of these crystallites possesses an anisotropic structure as with a crystal except that the boundary planes of a crystallite do not correspond to the anisotropy of the inner structure. With non-metallic substances, carbon compounds, salts and silicates, the crystal centers formed by great supercooling of the melt do not as a rule grow to actual crystal polyhedra but to spherulites.

Metals crystallize only in polyhedra or in dendrites. The non-isomorphous impurities of the metals collect during crystallization on the surfaces of the polyhedra or the branches of the dendrites so that the grains formed are finally surrounded with more or less thin layers which contain the principal metallic impurities in the form of complex eutectics. If a dendritic structure occurs, it ordinarily disappears rapidly in the neighborhood of the melting point and out of each structure a single crystallite is formed. This process proceeds more certainly when the cold metal is deformed and again heated

(recrystallization). The final structure of metallic substances is always as shown in Fig. 1.

Inside of the polyhedral pattern there are evidences of a spherulite pattern but the entire grain is a crystal. The occurrence of glide planes by deformation of a conglomerate of crystallites is definite evidence that the crystallites do not possess a spherulitic structure but are polyhedral sections of homogeneous crystals so placed that they are differently oriented with respect to one another.

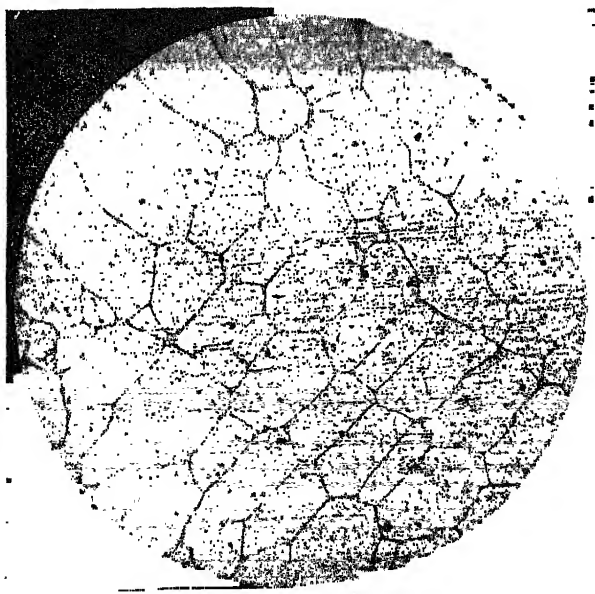


FIG. 1

Cast Copper. $\times 50$. Etched with $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$

Further evidence of the crystal structure of the crystallites is the formation of the etching pits on their sections. Fig. 2 shows a section of pure iron etched with alcoholic nitric acid and magnified 200 times. Invisible etching pits have formed on the individual grains whose form and position change with the orientation of the section through the crystallites. It is however the same over the entire section of a single crystallite. The intensity of the reflected light therefore changes from crystallite to crystallite.

If a piece of metal is broken at ordinary temperature the path of the rupture is often through the crystallites; the substance between the crystallites appears stronger than the grains. At higher temperatures the path is through the interstitial substances, since as complex

eutectics they naturally become partially liquid at relatively low temperatures and their strength is thereby much lowered.

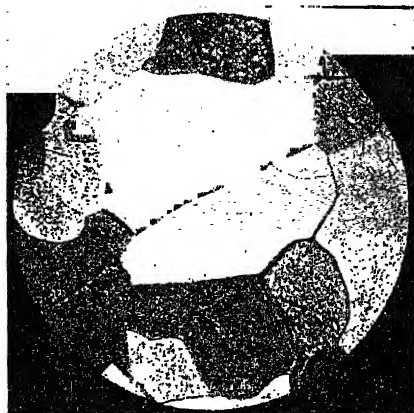


FIG. 2

Pure Iron. $\times 200$. (Oberhoffer.)

To prove the presence of the interstitial substance between the grains a solvent medium is used which is transparent and by whose action there is no gas evolution.

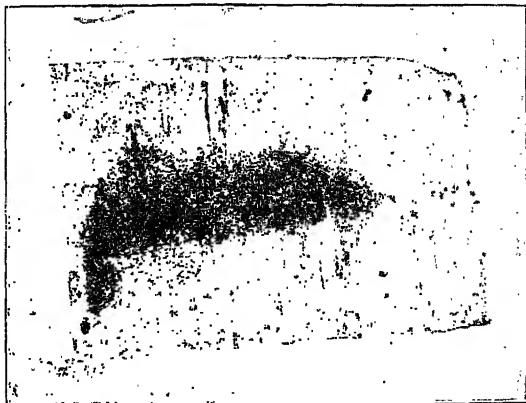


FIG. 3

If a cadmium sheet 0.1 to 0.2 mm. thick is immersed in an ice cold solution of NH_4NO_3 (50%) there appear after a few seconds fine seams of the interstitial substance forming a very fine, easily moved

network. The structure of this coating is best seen where it adheres to the bottom of the glass dish as it is thereby held in permanent tension. At these places it can be seen easily that we are not dealing with a coating but with a network in whose meshes the crystal grains were previously found.

If a piece of cadmium sheet of the same dimensions is dissolved in hydrochloric acid there remain irregular flocks and the mass of the interstitial substance appears less. The solution itself, however, is turbid from the fine particles of the interstitial substance. By gas evolution the interstitial substance is broken up.



FIG. 4

Fig. 3 shows a hard cadmium sheet of 0.04 mm. thickness after the solution. The remainder of the metal is in the form of black particles principally to be seen in the center. The fine web of the interstitial substance has practically the original dimensions of the cadmium strip. The direction of rolling is up and down. A part of the same strip was recrystallized at 250° and placed in a solution of 50% NH_4NO_3 . The direction of rolling here is from left to right (Fig. 4). The black flecks correspond to the undissolved cadmium crystallites.

2. The Tendency for Spontaneous Crystallization and Glass Formation.

Two Factors, the tendency toward spontaneous crystallization and the linear crystallization velocity, have an influence on the size of the grains of conglomerates of crystallites. Both depend on the temperature of supercooling of the melt. While the effect of temperature cannot be directly followed in opaque metal melts, a conception of this can be obtained by investigating other substances. The change

of the grain size in metals crystallized with different rates of cooling may then be investigated.

The formation of a new phase in one already present always takes place at first only in small areas whose number is very small in relation to the total number of molecules present. The point origin of new phases can be conceived of as a demonstration of the atomistic structure of matter. In supercooled liquids elementary crystals of unknown size are formed. It can be assumed that the first moment of formation of an elementary crystal is reached when the number of molecules or atoms is that necessary to occupy an element of the space lattice and in such a position relative to each other that they occupy the points of this space lattice element. It is however not sufficient for crystallization that a liquid accidentally possesses a constellation of molecules such that their arrangement corresponds to a space lattice element. The molecules themselves must change their condition, they must become anisotropic with the evolution of energy and the origin of polar forces in or about them which hold the anisotropic molecules together in a space lattice. A very small amount of the crystalline substance or of an isomorphous crystal placed in a supercooled liquid induces crystallization. From this it follows that an anisotropic molecule by its influence will cause isotropic molecules to become anisotropic and they will then seek the equilibrium positions in the space lattice corresponding to their anisotropic condition.

The number of crystallization centers which form in a unit volume in a unit time measures the tendency to spontaneous crystallization. This number we will call the nuclei number (Kernzahl, K. Z.). For non-metallic substances the relation of the nuclei number to the temperature of supercooling of the melt has been determined. For a series of substances it has been shown (*Kristallisieren und Schmelzen*, Leipzig, J. A. Barth (1903), p. 148, and also *Z. physik. Chem.* 25, 441 (1898)) that the nuclei number reaches a maximum by supercooling about 70-100° and by greater supercooling falls to the zero value. Thus, by great supercooling, many substances lose the ability to crystallize spontaneously and it may be assumed that this relation is entirely general, although it cannot be proven for every substance. However, if the linear crystallization velocity and also the nuclei number are large, it is not possible to cool the liquid substance so rapidly from the melting point that the temperature range of decreasing nuclei number will be reached before it is completely crystallized.

A liquid that is brought into the temperature region of decreasing nuclei number, i.e. below its temperature of maximum nuclei number, has its character greatly changed. It becomes a brittle glass. If this glass is heated either devitrification takes place which is no more than the beginning of crystallization or, the glass softens in a definite temperature interval and goes from a condition of high viscosity to one of ordinary liquid viscosity. The latter will take place

if the nuclei number becomes appreciable (*Z. Electrochem.* 10. 532 (1904)) only in the region of slight viscosity.

In such cases it has been shown that the heat content and the volume vary continuously through the temperature interval of softening, e.g. with betol the coefficient of expansion does not alter in this interval. It may be assumed (*Z. physik. Chem.* 28, 31 (1899)) that the optical properties, the dielectric constant, etc., also alter continuously in the softening interval. Only the viscosity changes in a way that resembles a discontinuous change; within a few degrees the

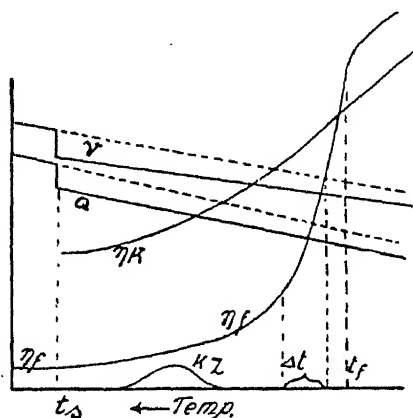


FIG. 5

mobility of the liquid is lost and it becomes solid. Fig. 5 shows the relation between change of heat content Q , the volume V , the viscosity of the liquid η^l and the viscosity of the crystalline substance η^k . At the melting point the volume and heat content change discontinuously. Simultaneously the viscosity of the crystals falls discontinuously to the viscosity of the liquid. The curve $K.Z.$ shows the relation between nuclei number and temperature. Δt is the softening interval in which the viscosity increases with extraordinary rapidity. It appears that if at the temperature t^l a certain high limiting value η of the viscosity is reached a further lowering of temperature does not change it markedly. The dotted lines show the volume and energy isobars of the supercooled liquid.

The softening of a glass is not to be confused with melting, and the softening interval of a glass has nothing to do with the melting point which is the equilibrium temperature of an anisotropic substance with its melt. While the process of melting an anisotropic substance is characterized by the absorption of the heat of fusion and a more or less great discontinuous change of a series of other properties as well as the viscosity, the softening interval has only

the decrease in viscosity in common with the melting process of an anisotropic substance.

There are also substances which at the temperature of the melting point have only slightly different viscosity for the crystals and the liquid. The η^i curve for these is greatly displaced towards the melting point. Such substances become isotropic but not liquid on melting. This phenomenon is exhibited by the feldspars and their closely related silicates. Concerning the spontaneous crystallization of silicates the work of C. Doelter should be consulted. (*Physikalische Chemische Mineralogie* (1905), p. 112.)

3. The Working of Amorphous Masses.

The nature of the viscosity change with the temperature in the softening interval is of importance in the working of amorphous masses. Since glassy amorphous masses are brittle at low tempera-

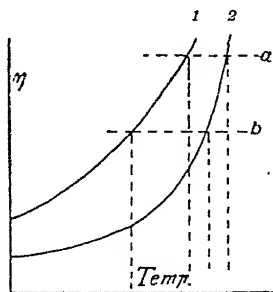


FIG. 6

tures, permanent deformation without rupture is not possible. On the other hand, as they are liquid at high temperature, it is often necessary for their working, that is, spinning into thin fibres or forming by the glass blowing process, that they have a certain especially favorable value of the viscosity or be within a certain interval of viscosity. For a given kind of working a definite absolute value of the viscosity is necessary which is the same for all vitreous substances, this value varying with the kind of work. For thin fibres the material must be kept within a smaller viscosity interval than for thicker fibres. The possibility of maintaining a definite viscosity value depends on the relation of the viscosity to the temperature. The viscosity curves 1 and 2 (Fig. 6) have different courses. The substance with a temperature function of viscosity corresponding to curve 1 is easier to work than the substance with the curve 2, since the requisite viscosity interval for working, a, b , is smaller for the second substance and it is therefore necessary to hold the temperature more closely.

The relative position of the zone of maximum nuclei number and the temperature interval in which the viscosity values are such that the form change may take place is of great importance in the shaping of amorphous vitreous masses. If the two are coincident, the hindrance from the process of devitrification is greater, the higher is the nuclei number.

Since the viscosity of a supercooled liquid always changes in such a way that it increases from small to very large values with decreasing temperature, the viscosity for all substances to be formed by the process of glass blowing must by its continuous change reach, at a certain temperature, the value favorable for forming. If, however,

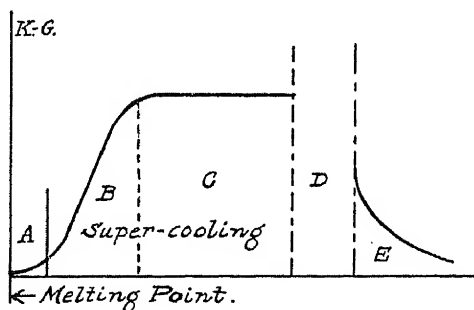


FIG. 7

the nuclei number and the linear crystallization rate are too large the substance crystallizes. Since on crystallization the viscosity suddenly increases, the viscosity curve of a crystalline substance is lacking a large number of viscosity values that are obtainable with an isotropic body. Experience teaches that the viscosity value necessary for forming tough masses may fall in the range of the viscosity drop on melting and accordingly in this case the material cannot be prepared for easy working. Therefore the same processes of shaping may not be used with crystalline masses (crystallite conglomerates) as with amorphous masses: glass, ebonite, celluloid, etc., and the same form changes brought about.

4. The Linear Crystallization Velocity (K-G).

If a liquid which readily undergoes supercooling, e.g. Benzophenon, is placed in a U tube and while at a temperature below its melting point is touched on the surface with a tiny crystal of the substance, it is seen that from the point of inoculation a series of crystal filaments grow in the liquid. They grow principally in the periphery of the tube. The ends of these fibres are faceted so that the boundary between them and the liquid appears slightly toothed. These visible crystallization boundaries move forward with a uniform velocity and

measurements have been made for many substances which show the relation of the K-G to the supercooling to be as depicted in Figs. 7 and 8. Fig. 7 gives the temperature relation of the K-G if the maximum value amounts to 5 mm. per minute and Fig. 8 if this value lies under 3 mm. With maximum velocities that lie between these values we get intermediate forms of the temperature relations between the types of Fig. 7 and Fig. 8. Five fields of supercooling may be distinguished for substances with a maximum K-G of more than 5 mm. per minute. In field A the K-G is very small and the crystals formed have a greater surface the less is the supercooling. In field B fibres that are closely parallel in direction grow in the peripheral part of the tube. In field C the inner part of the tube is filled with fibres that are closer together the greater the supercool-

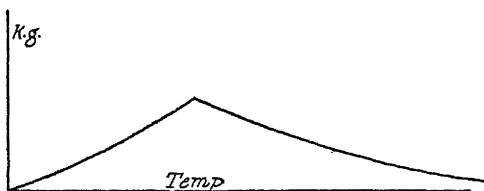


FIG. 8

ing. The crystallization boundaries in the greatest supercooling of the field C frequently appear as a convex reflecting meniscus since the entire amount of the supercooled liquid in the crystallization boundary crystallizes. In the field D a uniform velocity takes place only after the crystallization has proceeded for some time, since the observed initial velocities depend to a considerable degree on the diameter of the tube and the heat conductivity of the surroundings. Finally in the field E the K-G decreases very rapidly with decreasing temperature and soon falls to an inappreciable value.

In fields B and C liquid is still present between the crystal fibres; therefore, the crystallization boundary in these fields is presumably at the equilibrium temperature, i.e. the temperature of the melting point. This supposition is substantiated by the knowledge that in field C the K-G has a value independent of the supercooling.

In field B, however, the crystallization boundary is always at the equilibrium temperature and still the K-G increases with supercooling. The explanation of this fact is that in this field only relatively few crystal fibres grow and these principally near the tube walls. From this we conclude that in this field the K-G is smaller the slower the heat of crystallization is removed, and the K-G must accordingly decrease with increasing temperature since the heat of crystallization is removed more slowly the less is the temperature gradient at the crystallization boundary.

In field D the non-uniform velocity is explained by the explosion-

like nature of the process taking place. The heat of crystallization is no longer sufficient to raise the liquid to the melting point in the first moment since the supercooling is greater than the possible temperature increase $= \frac{\text{heat of fusion}}{\text{specific heat}}$. If the crystallization proceeds for a time, however, and the heat loss is small the layers at the recrystallization boundary will be heated and finally reach the melting temperature. In this field values of the K-G increasing with time may accordingly be observed.

Finally in field E, the K-G decreases with the temperature since the velocity of all molecular processes decreases with lowering temperature and it can be shown that the law which controls this relation is essentially in agreement with the law which relates chemical velocities to the temperature. (*Kristallisation Geschwindigkeit* IV, *Z. physik. Chem.* 81, 171 (1912).)

If the maximum K-G is small the heat liberated in unit time will also be small and it follows from this that in no field is the K-G independent of the amount of supercooling. The fields C and D are then missing from the curve which shows the relation of the K-G to the supercooling of the melt. Fig. 8 shows the course of the curve. In fields in which the K-G increases with increasing supercooling the crystallization boundary forms a concave meniscus. The K-G is increased by the heat extraction in these fields and since in the central portion of the tube the temperature gradient is smaller than in the peripheral part the crystallization boundary in the peripheral portion runs ahead of that in other portions. In the field E with decreasing K-G the crystallization boundary forms a convex meniscus, since in this field the K-G is lessened by heat extraction, and in the crystallization boundary the central part is at a higher temperature than the periphery.

Impurities lower the temperature of equilibrium between the melt and the crystals formed from it, if the impurities do not enter the crystals. Since with decreasing temperature the reaction velocity decreases it is to be expected that impurities greatly lower the K-G. These deductions have been confirmed experimentally.

For the linear transformation velocity of a meta-stable into a stable crystal form similar relations hold as for the K-G. (*Kristallisieren und Schmelzen*, p. 138, and A. H. R. Muller, *Z. physik. Chem.* 84, 177 (1914).)

5. The Nuclei Number and the Crystallization Rate Determine the Tendency of the Phases to Supercool.

The rate of cooling of a substance depends on its mass, its heat conductivity, its form, the temperature gradient to the surroundings and the heat conductivity of the surrounding substance. If a substance be brought into the supercooled state by rapid cooling, it must

obviously be brought to a temperature at which the nuclei number and the K-G are small in order to make it relatively stable. Whether the substance can be brought sufficiently quickly into this temperature range depends on the rate of cooling and also on the K-G and the nuclei number as well as on the relation between the nuclei number and the linear K-G.

When the maximum nuclei number occurs in the field of constant maximum K-G (curve 1 of Fig. 9) it is especially difficult to obtain the liquid as a glass; or if the curves refer to a reversible polymorphic transformation it is difficult to obtain a crystal form below its transformation point. It is the more difficult the greater the nuclei number and the greater the K-G. If both are large it is necessary to resort to a special quenching process as atomizing the melt into liquid air.

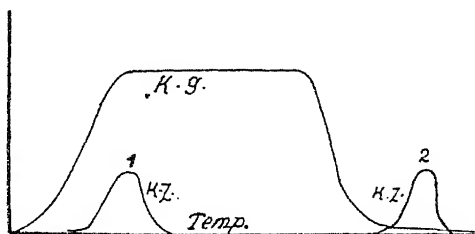


FIG. 9

If, however, the maximum nuclei number does not occur in the field of maximum K-G (curve 2) but in the field of very low values of the K-G, it is much easier to obtain the desired phase, at least in part, by quick cooling into the region below curve 2. Supercooling is always favored when one of the two factors, either the K-G or the nuclei number, are small. Supercooling is naturally easiest to obtain when both factors are small.

The tendency for metals to supercool is not important and the number of centers increases very rapidly with supercooling. It has not, therefore, been possible by quick cooling to obtain a liquid metal in the vitreous condition. On the other hand, a series of metallic crystals, especially solid solutions that are stable only at high temperatures, may be obtained as meta-stable bodies at ordinary temperatures by quenching. On heating these go over easily to the form which is stable at low temperatures. Impurities play an important part here. Pure β iron cannot be retained in this form at ordinary temperatures by quenching. By addition of carbon a meta-stable form may be obtained on quenching but this is not β iron, this form only being obtained by the addition of manganese. We are dealing here with a lowering of the number of centers and the linear transformation velocity by additions.

6. The Preparation of Long Cylindrical Crystals by Slow Crystallization of the Melt.

In the field A, Fig. 7, the K-G decreases rapidly with decreasing supercooling. In this field there are formed as a rule not crystal fibres but many faceted polyhedra. If crystallization is allowed to proceed in a narrow tube up to 1.5 mm. diameter with a supercooling of $1-3^{\circ}$ the crystallization proceeds from the closed end and slowly the entire tube is filled with a single crystal. The crystal cylinder frequently has the same orientation throughout its entire length and only seldom contains vacuoles. This process makes it possible to prepare homogeneous crystal cylinders of any desired length. These crystal cylinders are not only physically but chemically homogeneous since impurities are less taken into the crystals the slower the cooling and accordingly remain entirely in the melt. This is known from the fact that coloring matters which only slightly colored the melt are enriched, turbidity from precipitation of water and other substances occurs and the K-G in the upper part of the tube is greatly lessened since the equilibrium temperature between the crystals and the melt is lowered by impurities.

That the value of the K-G has a great influence on the adsorption of impurities in a crystal so formed may be demonstrated in the following way. If various dyes are added to liquid benzophenone and the melt inoculated in one case $1-2^{\circ}$ below the m.p. (48°) and in another case 30° below the m.p. colorless crystals surrounded by colored fringes are formed in the first preparation and in the second case slightly colored crystals.

This process (H. Block, *Z. physik. Chem.* 78, 385 (1911)) for the preparation of chemically or physically homogeneous crystals, may be used, e.g. for the determination of the volume change on melting. Further, this process of purifying metals and developing metal fibres of a single crystallographic orientation is of special importance, since on such metal fibres the physical properties of the metal which are of a vectorial nature as the electric conductivity, the thermo-electric force and the elastic properties may be measured much more precisely than on a quasi-isotropic conglomerate of crystallites. That such experiments are feasible is shown by an experiment with bismuth. A piece of bismuth 20 cm. long was obtained by very slow cooling whose cleavage faces throughout the entire length had the same angle to the tube axis.

7. Size of Crystals in Conglomerates Obtained by Cooling the Melts.

The number of crystallites can be determined in metals by preparing a section and properly etching it to bring out the polygonal outlines and counting the polygons (crystallites) that a known area of

the section contains. If we designate the number of polygons n in the area of the section q measured in sq. cm., the number of crystallites in 1 c.c. is

$$N = \left(\frac{n}{q} \right)^{3/2}$$

Great differences in the size of the polygons indicate that the nuclei number at the temperature at which spontaneous crystallization took place was small since with small nuclei number the separation of the crystallization centers from each other is dependent on chance. If at the same time the K-G is large the grains will be of very different sizes. If with small nuclei number the K-G is also small the difference in size of grains is less the smaller the K-G since with smaller values of the K-G the time of crystallization is increased. A small uniform grain indicates a large nuclei number while inequality of grains is produced by a small nuclei number.

The determination of N gives us a conception of the magnitude of the nuclei number but not its actual value. N does not have a simple relation to the nuclei number, which is the number of crystallization centers formed in unit time and volume at constant temperature. During crystallization these parameters change. The relation of N to the nuclei number accordingly involves a volume integral.

By carrying out a series of quenching experiments with the same substance it is possible by determining the crystallite number N to get an idea of the relation between the temperature and the K-G and nuclei number. We may write the equation $N = f \frac{\text{Nuclei number}}{\text{K-G}}$

and if we assume that the factor f does not appreciably change with the degree of quenching we may conclude that if N increases with the degree of quenching then with decreasing temperature the relative increase in nuclei number overbalances that of the K-G. The grain size accordingly decreases with increasing degree of quenching. If the grain size increases with the degree of quenching it must be concluded that the relative change of the K-G overbalances that of the nuclei number.

If it is assumed that in the given quenching interval the K-G still possesses its constant maximum value during the principal part of the time of crystallization, a decrease of N with increasing degree of quenching means that the nuclei number itself decreases with decreasing temperature.

An experiment in this direction has been made by E. Bekier. (*Z. anorg. Chem.* 78, 178 (1912).) He found that with bismuth the number of crystallites per unit of volume increased with the degree of quenching while with antimony under the same conditions he found a very noticeable decrease of the crystallite number with increase of the degree of quenching.

8. Surface Tension in Lamellæ of Solid Bodies.

If lamellæ of various thickness are heated, e.g. gold leaf or glass lamellæ, they begin to buckle at a definite temperature. The temperature of buckling increases with the thickness of the lamellæ. The surface tension α of an isotropic solid body may be determined in the following way. Let the absolute strength of the lamella of thickness d per 1 cm. width be f grams. This strength is proportional to the lamellar thickness. If a lamella is heated to a temperature T_s where $f = 2\alpha$ the lamella begins to buckle. If the surface tension α decreases more slowly with increasing temperature than the strength f , the temperature of buckling increases with lamellar thickness, as is seen in Fig. 10. The lines f , d and f_2 , d_2 give the relation between lamellar strength and temperature; with increasing thickness the

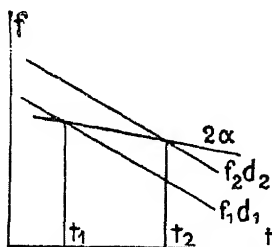


FIG. 10

strength increases. The intersections of the line 2α which give the relation of the surface tension to the temperature, with the lines f , d , and f_2 , d_2 are at the temperatures of buckling. It is seen that with increasing thickness the buckling temperature must increase if the strength and the surface tension change with the temperature in the way given. The relation of the strength to the temperature for lamellæ of various thicknesses is known so that the line for the surface tension 2α may be constructed on the basis of buckling temperature.

The relations are not so simple with metal lamellæ as with glass lamellæ, e.g. if gold is rolled and hammered out to a thin sheet, glide planes are formed in it which are not present in the glass. When the above relation is determined the glide planes act as free surfaces and contribute to the buckling force. According to the determinations of H. Schottky (*Nachr. d. k. Ges. d. Wiss. zu Göttingen* (1912), p. 480) this force for sheet silver of .19 μ thickness is 10 g. per cm. of width at 300° and for sheet silver 0.7 μ thickness is 33 g. at 400°. If the buckling were only due to the force on the lamella surface, the buckling force would be independent of the lamella thickness. Since it is, however, nearly proportional to the thickness the glide planes must act to the contrary. For a metal lamella the simple buckling relation for an isotropic substance $f_{T_s} = 2\alpha$ does not hold

and the complex one, $2na_1 + 2a = f_{T_s}$ where a is the surface tension, a_1 the tension in the glide planes, N their number and f_{T_s} the lamellar strength at the buckling temperature T_{s1} must be substituted.

The buckling force in sheet silver is considerably greater than the surface tension of a liquid. The surface tension for mercury at 18° is 55 g. and for H_2O is only 0.075 g. per cm.

9. The Form of Crystals Grown in the Melt.

Under conditions of slight supercooling, crystals grow in their melts as many faceted polyhedra; with greater supercooling, however, they grow as crystal fibres. If the substance is deposited quickly on a crystal already present crystal fibres are obtained; if however it takes place slowly many faceted polyhedra result. This fact is also met in the formation of crystals from solutions.

The linear K-G is obviously a vector; if it were not, crystals would be bounded by spherical surfaces. Every bounding surface of the crystal has a definite vector of the linear K-G; it is vertical to the boundary plane of the crystal which owes its origin to this vector and the distance of the different boundary planes from the centre of the crystal is proportional to the K-G in the direction normal to the plane.

P. Curie sought to refer the polyhedral form of crystals to the surface tension of their boundary planes. It is, however, not clear how the surface tension, so long as the solidity is not exceeded, has an influence on the crystal form. In any case the influence of surface tension on the shape of a crystal would be entirely different than Curie has assumed. Its action would produce not polyhedra but triaxial ellipsoids, rotation ellipsoids or complex forms.

While the surface tension of liquids is evidenced by capillary phenomena, it cannot be evident in crystals so long as the surface energy does not exceed the solidifying force f .

If for a given substance f -a passes through zero at a temperature below the melting point, this substance at temperatures where f -a is negative does not crystallize in polyhedra but in rounded crystallites whose surfaces are continuously curved. The same substance will crystallize in polyhedra if its precipitation temperature is such that f -a is positive. Also intermediate forms between polyhedra and forms with continuously curved surfaces are possible.

For a series of metallic substances the temperature at which $f < a$ is below the melting point. Hence we frequently meet in metallic conglomerates, crystallites whose intersections with a plane through their bounding surfaces are closed curves. Crystals with spherical and ellipsoidal bounding surfaces are obviously not to be considered as spherulites which consist of needles radiating out from a point, such a structure has not yet been recognized in a metallic conglomerate. In any case if such did occur they would be recognized in part by

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their radial fibrous structure. Concerning metals and metal compounds, we may assert that their precipitation from binary melts is at least as frequent in non-polyhedral form as in polyhedral form. For these substances then the condition $f-a=0$ is frequently fulfilled at temperatures below that of crystallization, while with many silicates and most organic substances that is not the case, since they crystallize only in the polyhedral form. The influence of temperature on the form of metallic crystals is shown very nicely by copper which has been crystallized out of its liquid mixtures with bismuth.

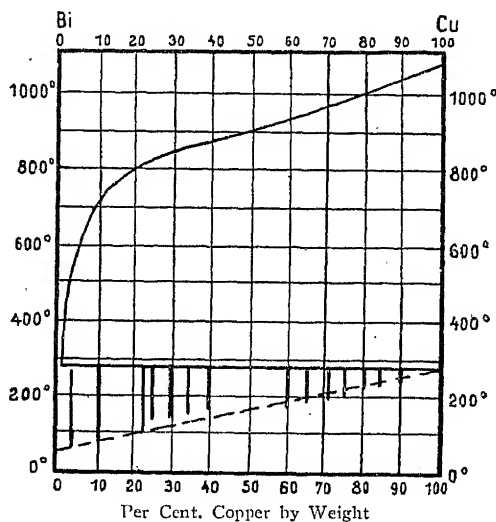


FIG. 11

The curve for the commencing of crystallization of copper out of Cu-Bi melts runs as shown in Fig. 11 from 1080° to 280° . From all melts that contain more than 1 per cent. copper practically pure Cu crystallizes. From melts with 50 per cent. Cu the greatest part of the copper crystallizes between 900° and 800° while from melts with 25 per cent. copper the greatest part between 800° and 700° . From microscopic investigations we find that the Cu crystals formed between 900° and 800° or at higher temperatures are rounded (Fig. 12) while below 800° the crystals and crystal skeletons have polyhedral form (Fig. 13). Also in Fig. 13 there are still some rounded crystallites and crystal skeletons which during their formation were strongly curved by the influence of surface tension.

Beryllium crystallized from liquid mixtures with Ag or Al (Oesterheld, *Z. anorg. Chem.* 97, 27 (1916)) is a further example of the dependence of crystal form on the temperature.

Crystals of the compound FeSi whose crystallization curve extends over a considerable temperature interval are also rounded if formed at high temperatures while those formed at lower temperatures are polyhedral.

10. Is the Granular Structure of Metallic Structural Materials Especially Favorable to their Mechanical Properties?

From consideration of experiments made on rocks we may conclude that the best mechanical properties are not obtained with a

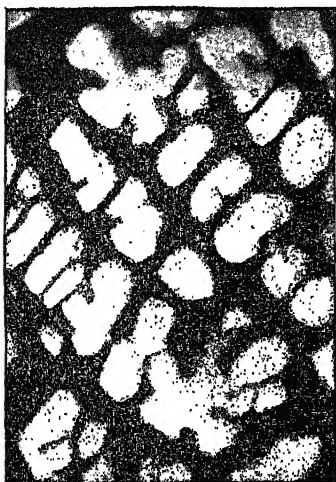


FIG. 12
50% Cu, 50% Bi. $\times 180$

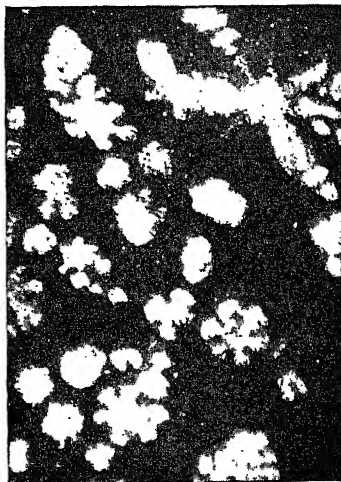


FIG. 13
25% Cu, 75% Bi. $\times 180$

granular structure but with an unoriented fibrous structure. In general rocks have a granular structure; nephrite and jadite, however, are characterized by a fibrous structure. Compression and impact tests show these rocks to be very much stronger than granular rocks of the same chemical composition. (Doelter, *Handb. d. Mineralchemie*, II (1) pp. 670 ff.

The grain size of metallic structural materials can be lessened by rapid extraction of heat during their crystallization, their structure however remaining granular. Wrought iron and other cold forged or rolled materials have an oriented fibrous structure; an unoriented fibrous structure cannot be obtained with metals since there is no means of changing the ratio of the K-G vectors.

II. The Space Lattices of Metals.

Concerning the crystal form of metals we were until recently very poorly informed since the preparation of well-formed crystals was a matter of considerable difficulty. Through the discovery of Laue and the subsequent work of the Braggs, of Vegard and of Debye and Scherrer we are an unhopd-for step nearer being able to determine the kind of space lattice and the spacing of the lattice points for metals. The knowledge of these things is incomparably more important than that of the outer form, which is influenced by conditions of formation. At the present time the space lattice is known for only a few metals. One can predict from this knowledge, however, the formation of continuous series of solid solutions.

The metals which form a continuous series of solid solutions have the same kind of space lattice; the spacing of their lattice points may, however, vary a little from each other. On the other hand two bodies with the same kind of space lattice need not form a continuous series of solid solutions. For a continuous series of solid solutions the similarity of the space lattice is only one condition, the second is that the attractive forces between the two kinds of atoms or molecules be sufficient. The nearer the equality of the spacing of the lattice points, the less is the importance of this latter qualification.

The lattice of the following metals is the 14-point lattice (a cubic lattice with atoms in the cube corners and face centers). The length of the cube sides for several metals is as follows.

Cu	3.61×10^{-8} cm.	Al	4.07×10^{-8} cm.
Ag	4.08×10^{-8} cm.	Ni	3.53×10^{-8} cm.
Au	4.07×10^{-8} cm.	γ Fe.....	3.60×10^{-8} cm.
Pb	4.91×10^{-8} cm.	Tl	5.12×10^{-8} cm.

Besides these the lattices for As, Sb, and Bi are known. Their atoms have two interpenetrating rhombohedral lattices. The lattice for Si is like diamond; that of W is cubic with the corners and cube center having W atoms; and the lattice of Mg consists of two interpenetrating hexagonal lattices (H. Bohlin, *Ann. Phys.* 61, 421 (1920)).

Continuous series of solid solutions are known for the following metal pairs, Cu-Au, Ag-Au, Cu-Pd, Ag-Pd, Au-Pd, Cu-Pt, Cu-Ni, Cu-Mn, Ni-Mn, Co-Mn, Fe-Mn, Fe-V, and Ni-Co.

It follows from this that the atoms of the following metals possess a cubic lattice with atoms in the corners and the face centers.

V, Mn, γ Fe, α Co, α Ni, Cu Ru?, Rh?, Pd, Ag, Os?, Ir?, Pt, Au.

These metals can be recognized as the middle ones in the periodic system. It is remarkable that nearly all the technically important metals have the same lattice. Exceptions are Zn, Cd, and Mg, which are hexagonal and ordinary Sn which is tetragonal.

[The study of the crystal structure of metals has made rapid progress in the last few years and today the crystal structure has been determined for practically all metals. A very considerable portion of this work has been done by A. W. Hull (*J. Am. Inst. Elec. Eng.* 2, 1171 (1919), *Phys. Rev.* 17, 571 (1921), *Phys. Rev.* 20, 113 (1922), *Phys. Rev.* 18, 38 (1921)). The structure of the various metals may be grouped somewhat as follows: Cubic face centered, Al, Co, Ni, Cu, Rh, Ag, Pt, Au, Pb, Ca, Sn (gray), Ce, Ir, γ Fe. Cube centered Li, Na, Cr, α Fe, Mo, W, Ti, Ta, K, V. Hexagonal close packed, Mg, Zn, Cd, β Co, In, Ru, Be, Hg. Ordinary tin is tetragonal, antimony is hexagonal with two interpenetrating face centered lattices, bismuth is rhombohedral. (L. W. McKeehan, *J. Frank. Inst.* 195, 59 (1923).) R. S. D.]

B. Change of Properties with Change of State

To obtain the most comprehensive possible survey of the relation of the properties of a chemically homogeneous substance to the temperature T and pressure p we conceive of lines erected normal to the p - T plane, whose lengths are proportional to the given properties of the substance. If a surface is passed through the ends of these vertical lines it gives us a complete picture of the relation of the property under consideration to the temperature and pressure. In these property-surfaces we find discontinuities in part of the properties and in others only changes of direction. If property-surfaces are constructed over the same p - T plane for all properties of a given substance and the discontinuities and direction changes are projected on it, we get a series of curves on the p - T plane and the projection of every property-surface gives the same curves. The projections of the discontinuities or direction changes accordingly are coincident, the same curve is therefore obtained no matter what property surface is used. These p - T curves obviously have a special meaning in regard to property changes as well as in other respects. Since at points on these curves the equation for the property in relation to the temperature at constant pressure or in relation to the pressure at constant temperature, changes suddenly, some special process must go on in the structure of the substance itself. This process is, we learn further, the loss of the physical homogeneity of the substance; that is, its separation into two parts. These two parts, the two phases, are in equilibrium with each other at all points of the same p - T curve.

The occurrence of heterogeneity and the occurrence of discontinuities or changes of direction in the property-surfaces are caused by the same conditions. These phenomena are atomic in that the molecular distribution in space is different in different phases. So long as the substance is homogeneous its properties and their differential quotients toward p and T change continuously since its atomic structure changes

continuously. If however the atomic structure changes discontinuously the properties, or at least their derivatives with respect to p and T , change discontinuously.

1. The Equilibrium Diagram.

Fig. 14 shows the equilibrium curves on the p - T plane for an ideal substance. The equilibrium curves separate the fields of existence of the vapor d , the liquid f and crystal state k . It is seen that the

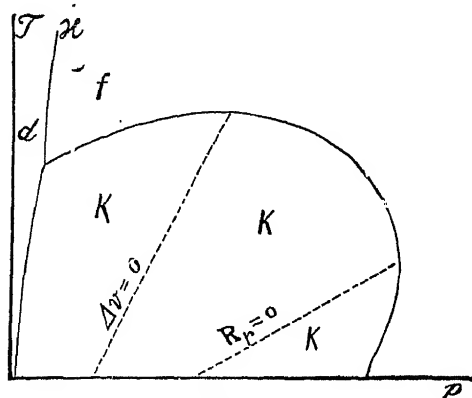


FIG. 14

fields of existence for vapor and liquid are only partially separated from each other, and that obviously the pressure and temperature of a substance in the liquid state may be so altered that the vapor pressure curve is not crossed and yet the substance comes into the liquid field. Above the critical point \propto the fields d and f come together. The liquid can accordingly be changed to vapor and vice versa without a discontinuous change at any time.

The explanation of this is that the molecular arrangement is practically the same in the vapor and liquid, that is, absolute disorder, and that only the distance apart of the molecules in the vapor and liquid is different. At the critical point \propto this becomes equal and the difference in energy content of the vapor and the liquid vanishes since the molecular structure is identical in both.*

* Parts of the vapor pressure curves of metals were first measured by C. Barus. (*Messung hoher Temperaturen*, J. A. Barth, Leipzig, 1892.)

At temperatures considerably below the melting point the vapor pressure is vanishingly small. A very large temperature increase therefore corresponds to a very small pressure increase. If a metal is heated to boiling in a highly evacuated tube, the boiling point of the metal increases greatly with the height of the column of vapor above the metal since the small pressure increase raises the boiling point of the metal. A noticeable distillation takes place in high vacua at relatively low temperatures. F. Krafft observed (*Berl. Ber.* 36, 1690

The relations on melting or crystallizing are entirely different. Since in a crystal the molecules are arranged according to a space lattice, and this arrangement is apparent since a part of the crystal properties depend on the direction in the crystal, naturally the crystal cannot be melted without a discontinuous change in at least one of its properties. From the arrangement in a space lattice to absolute disorder of the molecules there is obviously a gap in molecular arrangement. Therefore the field of existence of the crystal state must be separated from the fields of the isotropic states, the vapor and the liquid. Since with increasing temperature the kinetic energy of the molecules increases, it is very improbable that the equilibrium curve, the melting curve, increases to very high temperatures since the forces holding the space lattice together would have to increase very much. It is probable that with increasing pressure the melting curve either becomes asymptotic to a maximum temperature or by sufficient pressure rises to a maximum melting temperature, and then falls with higher pressure.

A comprehensive theoretical investigation shows that if the volume difference Δv for a crystal and its melt passes through the zero value with sufficient pressure, there must be two equilibrium pressures at the same temperature. To agree with these stipulations the melting point curve must accordingly have a maximum. At this maximum $\Delta v = 0$, and no discontinuous volume change takes place on melting while at all other points on the melting curve the volume changes discontinuously on melting. Below the pressure of the maximum melting point the volume increases discontinuously on melting; above this pressure it decreases discontinuously.

The volume difference Δv however not only passes through the zero value at one point on the melting curve, but also in a series of other points inside the field of existence for crystallized material. These points lie on the neutral curve $\Delta v = 0$ (Fig. 14). If a supercooled liquid crystallizes at a point on this curve, no volume change takes place. The intersection of this neutral curve with the melting

(1903)) such distillation with Zn at 300°, with Cd at 320°, with Sb at 670°, with Bi at 540°, with Ag at 1200°, with Cu at 1315°, and with Au at 1375°. The following table gives a summary of the boiling points of metals at a pressure of 1 atmosphere.

Cd	D. Berthelot	778°	Ag	{v. Wartenberg	2070°
Zn	"	918°		{Greenwood	1955°
Mg	{Ditte	1100°	Al	"	1800°
	{Greenwood	1120°	Mn	"	1900°
Sb	{Meusching, v. Meyer..	1437°	Cr	"	2200°
	{Greenwood	1440°	Sn	{v. Wartenberg	> 2200°
Bi	{Barus	1550°		{Greenwood	2275°
	{Greenwood	1420°	Cu	{v. Wartenberg	> 2200°
	{Ruff	1490°		{Greenwood	2310°
Pb	{Greenwood	1525°		{Ruff	2305°
	{Ruff	1555°	Fe	Greenwood	2450°
			Au	Ruff	2600°

curve is distinguished from all other points on the neutral curve by the fact that at it the transformation of the isotropic phase to the anisotropic is reversible, while at the other points of the neutral curve only the isotropic can change to the anisotropic. This point represents the maximum melting temperature of the substance. The melting curve is represented by the equation $\frac{dt}{dp} = \frac{\Delta v T}{R_p}$. Then since $\Delta v = 0$ when the heat of fusion R_p possesses a finite value, the tangent to the melting curve at its intersection with the neutral curve will run parallel to the p -axis, this point is accordingly the maximum of the melting curve.

One other neutral curve, where the heat of fusion R_p goes through the zero value is indicated by the line $R_p = 0$ (Fig. 14). The intersection of this curve with the melting curve gives the maximum

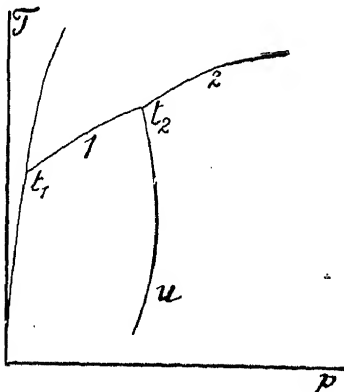


FIG. 15

pressure of melting. At this point the tangent to the melting curve runs parallel to the T axis since in the above equation $R_p = 0$, when the numerator $\Delta v T$ has a finite value. The further course of the equilibrium curve between anisotropic and isotropic substances is determined by the Nernst heat theorem that R_p vanishes at absolute zero; hence $\frac{dt}{dp}$ is a second time infinitely large at $T = 0$.

The pressure of the maximum melting point is very different for different substances. For metals it is always very high; to give a number, well over 50,000 kg. per sq. cm.

Experience has taught that very frequently not only one but many crystal forms crystallize from a liquid, each differing in its properties, volume, heat content, etc. These crystal forms may be divided into two groups on the basis of their conditions of stability. To one group belong the totally meta-stable forms; to the other the partially

meta-stable. The melting curves for the totally meta-stable forms do not intersect the melting curve for the stable form, but run inside of the field of existence of the stable form; on the other hand the melting curves of two partially stable forms intersect, 1 and 2 (Fig. 15). From this intersection a third equilibrium curve originates ut_2 where both partially stable forms are in equilibrium (transition curve). This triple point t_2 is in many ways analogous to the triple point t_1 , since in point t_1 , three phases, vapor, liquid and one crystal form, are in equilibrium with each other and in triple point t_2 the liquid and both crystal forms 1 and 2 are in equilibrium with each other. Besides the two crystal forms 1 and 2, each of which has a field of stable existence totally meta-stable forms may occur. As deduced from the theory (*Zur Thermodynamik der Einstoff Systeme*, II *Ann. Phys.* 40, 297 (1913)) and substantiated by experiment (*Z. physik. Chem.* 84, 257 (1913), and F. Körber, *Z. physik. Chem.* 82, 45 (1913)), the equilibrium curves of these meta-stable forms run somewhat parallel to the equilibrium curves of the stable phases, consequently they never intersect each other (Fig. 15). The equilibrium curves of some meta-stable forms accordingly fall in the field of existence of crystal form 1 and that for other meta-stable forms in the field of existence of crystal form 2. From these facts we may conclude that there is a closer relationship between the equations of state of those forms whose equilibrium curves do not intersect than between the equations of state of forms whose equilibrium curves intersect. The meta-stable forms accordingly align themselves either with crystal form 1, or crystal form 2. Such a group of crystal forms of different stability is characterized in that its equilibrium curves with other phases do not intersect one another. Besides this characteristic there are still other characteristics which place two crystal forms in the same group. If the volume of the meta-stable form is greater than that of the stable form and the reverse relation holds for the heat of fusion, the two forms in all probability do not belong to the same group.

Further we find from experience that from normal liquids, i.e. those which as judged from their temperature coefficient of surface tension, their heat of vaporization and the heat of fusion of crystals formed from them, consist of one kind of molecules only, one group of forms crystallizes, while from liquids which on the basis of their properties are to be considered as mixtures of different molecules, as a rule two or more groups of forms crystallize. Atomically these processes take place in the following way:

The forms of various stability of the same group of a normal liquid are built from one and the same kind of molecules and possess different space lattices corresponding to different stabilities. The same obviously holds for the forms of a group resulting from associated liquids. On the other hand the forms of different groups that originate only in associated liquids are built out of different kinds of molecules, which may possess the same or different space lattices. The

forms of a given group due to their different stabilities cannot be in equilibrium with each other, since for the various space lattice arrangements of the same kind of molecules there is apparently a definite field of stability which, for the stable form, includes the entire field of existence. If on the other hand two forms may be brought into equilibrium the conditions must be such that at the surface of contact of the two forms as many molecules of one form change into the other in unit time as vice versa.

The occurrence of transition curves in the equilibrium diagram, whose existence is established by the discovery of a transition point, shows that the substance under consideration can exist as two kinds of molecules. These kinds of molecules may be related to each other as polymers or isomers.

Transition points have been found for many substances in recent years, especially among those substances containing the hydroxyl group and among many salts. We will consider here only the transition points that have been found for metals. The occurrence of transition points in the chemical elements is related to their position in the periodic system, and depends accordingly on the inner structure of the atoms.

The ferromagnetic metals:

Fe Co Ni

that belong to a natural group in a narrow sense are characterized by transition points. These are at the following temperatures:

Fe	769° 906° 1401°	Co	1150°	Ni	350°
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At the transition points of iron discontinuities occur in the heat content. The volume change at 769° is not noticeable (Lechatelier & Charpy); with rising temperature a noticeable contraction of iron takes place at 906°; nothing is known concerning the volume change at 1401°. The transition of nickel is accompanied by a very small discontinuous change in the heat content (Baykow), but the volume change cannot be detected. With cobalt the change of heat content and the change of volume have not been measured, but probably are quite small. The property that changes especially with iron at 769°, with Co at 1150°, and with Ni at 350° is the magnetic permeability.

In other natural groups of the periodic system transition points are known for most, if not all, of the members. We will consider here the natural groups of C and Ge

C Si Ti Zr Sn Pb. Th

For carbon there must be a transition curve where graphite and diamond are in equilibrium with each other, its position in the p - T

plane, however, is unknown. Silicon crystallizes with a volume increase, being in this respect similar to water and bismuth. Liquid silicon is accordingly in all probability an associated liquid, and a transition point in crystallized silicon is to be expected. In fact Königsberger and Schilling (*Ann. Physik.* 32, 179 (1910)), found that the electrical resistance of silicon changes reversibly and discontinuously at 214° and 435° . A similar change is found in titanium at 310° .

With Zr, Th and Ge it appears that transition points have not been sought. Two transition points are found for Sn, one at 18° (E. Cohen, *Z. physik. Chem.* 30, 61 (1899); 33, 57; 35, 588 (1900); 36, 513 (1901); 48, 243 (1904)), and one at 161° (M. Werner, *Z. anorg. Chem.* 83, 275 (1913)). By the change of ordinary tin into the gray, which takes place with decreased density, wart-like spots are slowly

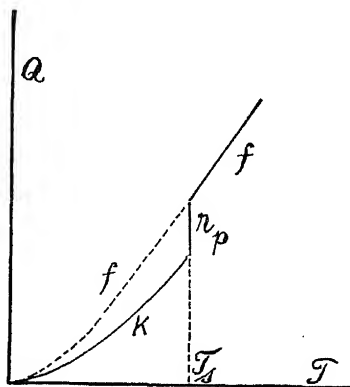


FIG. 16

formed (tin pests). On the other hand a transition point is not found in lead at low pressures.

Thallium has a transition point at 226° . At this point the heat content increases discontinuously while the volume and the electrical resistance decrease discontinuously. For the two rare metals of the thallium group, Ga and In, no investigations have been made in regard to the transition points.

Finally for zinc, a transition point is found at 304° , at which point the heat content changes discontinuously. From the curve which shows the relation of the electrical resistance to the temperature a discontinuous change is not found, but only a break at 310° . Breaks are also found (M. Werner, *Z. anorg. Chem.* 83, 275 (1913)) at 300° in the curves showing the relation of the thermo-electric force of zinc against platinum and iron to the temperature. No transformation points have been found for the two other metals of the zinc group.

2. Heat Content.

The specific heat of anisotropic bodies is only slightly dependent on the temperature at not too low temperatures. At low temperatures however the specific heat decreases, according to Nernst, in such a way that it may be assumed that the specific heat vanishes at absolute zero. The heat content Q of an anisotropic substance at a pressure, $p = 0$, and a temperature T is given by the summation $\int_0^T c_p dt$; c_p

represents the specific heat at constant pressure. Corresponding to the change of the specific heat with the temperature the heat content of a substance increases at first very slowly, and then more rapidly (curve K , Fig. 16) up to -100° and thereafter as a rule practically linearly with increasing temperature. At the melting point T_s , the heat content increases discontinuously; this increase is equal to the heat of fusion R_p . The heat content of the liquid (curve f) always increases faster than that of the crystalline substance. Also the curvature of the line representing the heat content of the liquid is greater than that of the line representing the heat content of the crystalline substance. This is probably due to the fact that the curvature of either line representing the heat content increases with increasing temperature. For the supercooled condition of the liquid the dotted extension of the curve f holds.

At the boiling point of the liquid the heat content increases again discontinuously since the heat of vaporization is taken up. The specific heat of the vapor c_p is smaller than that of the liquid. The relation between the specific heats c_p'' , c_p' and c_p , of a substance in the anisotropic, in the liquid and in the vapor state for temperatures above -100° , is given by

$$c_p'' < c_p' > c_p.$$

Further for the specific heat of the liquid and the crystalline substance in the neighborhood of the melting point T_s , the following relation holds

$$c_p' - c_p'' = \frac{R_p}{T_s}$$

accordingly the curves f and k (Fig. 16) are so directed at the melting point that the tangents to them intersect at $T = 0$.

For various metals in the anisotropic condition the curves of the heat content are practically coincident if they are considered not on the basis of unit of weight but on a mass which is proportional to the atomic weight, since for crystallized metals the law of Dulong and Petit holds and the deviations from it occur only at very low temperatures.

For the heat of fusion of metals the law of Crompton holds. This

law states that the atomic heat of fusion divided by the absolute temperature of the melting point has practically the same value for most metals, 2.0 calories. It may accordingly be said that the heat content of metals per gram atom in the crystalline state in relation to the temperature approximates a straight line and that of liquid metals a similar straight line which converges with the first at absolute zero. The distance between these two lines at the same temperature gives the atomic heat of fusion.

For compounds the heat content is, according to the Neumann-Kopp law, made up additively of the heat content of the components of the compound. For the heat of fusion of non-metallic substances if the substance consists of only one kind of molecules in the liquid state Walden has formulated the rule that the molecular heat of fusion

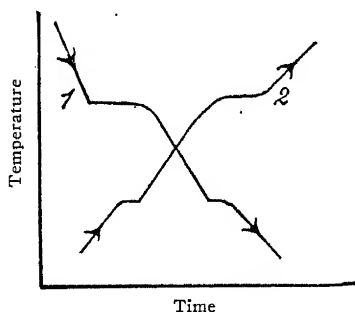


FIG. 17

divided by the absolute temperature of the melting point varies only slightly from 13.5 cal.

The exact determination of the heat content of a substance is a time consuming task. Since at the equilibrium temperature of a crystalline substance with its melt the heat of fusion is given out or taken up and similarly at the equilibrium temperature of two kinds of crystals, the transition point, the corresponding heat of transition is evolved or absorbed, these facts are used for the determination of the melting point or transition point. To this end the cooling curves or heating curves for the substance under investigation are used. If the melt is placed in a thermometric apparatus and the temperature observed through which it cools or heats in equal time intervals, arrests occur in the cooling curve at the temperature of the melting point and transition point, the temperature of the substance remaining unaltered for a time due to the liberation of the heat of crystallization or transition (curve 1, Fig. 17). In the heating curve (curve 2, Fig. 17) the same arrests occur. As a rule the temperatures of the arrests in the heating curve are somewhat higher than the arrests in the cooling curve since the thermometric apparatus requires

some time to reach the equilibrium temperature of the substance. The greater the mass of the thermometric apparatus the greater will this difference be.

It sometimes occurs that in the first cooling curve the arrest at the melting point is followed by a second arrest which, however, does not appear on the heating curve or if the substance is not melted in between, does not occur again on a cooling curve. In this case the transition is not reversible. The explanation is that a meta-stable crystal form has precipitated from the melt which at the temperature of the second arrest spontaneously goes over to a stable crystal form. Consequently the arrest is missing from the heating curve. This arrest is naturally missing on cooling and heating so long as the substance is not melted again.

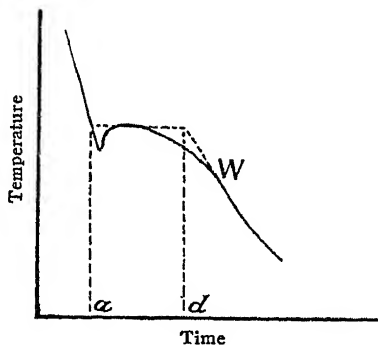


FIG. 18

If, however, by crystallization of the melt the meta-stable form is again precipitated the cooling curve will again show an arrest approximately at the temperature of the first arrest. In this way it may easily be decided whether the reaction which causes the arrest is reversible or irreversible, whether it is the transition of a meta-stable into a stable crystal form or whether it is the reversible transition of two crystal forms each of which is stable on one side of the transition point.

Figure 18 shows the form of an arrest which is frequently observed with chemically homogeneous metals. The crystallization takes place after a supercooling of from two to twenty degrees. Thereupon the temperature as measured by a thermo-element protected by a thin porcelain tube remains for a time entirely unaltered. Toward the end of the crystallization, however, the temperature begins to fall, faster at first, then in a normal way as the temperature of the surroundings is approached. At the boundary of the crystals and their melt a fixed temperature exists with a chemically homogeneous substance. However, during the crystallization, this boundary recedes further and further from the thermometer as crusts of crystals build

up between the thermometer and the crucible walls. The remainder of the melt accordingly crystallizes in a layer that lies between the thermometer and the crucible walls and surrounds the thermometer concentrically, and while it still crystallizes at the temperature of the melting point, the temperature of the thermometer falls at first slowly then more rapidly. The crystallization ends at the inflection in the cooling curve (Fig. 18). If the part of the cooling curve that refers to the cooling of the completely crystallized mass be prolonged above the point W and a parallel to the time axis passed through the constant temperature of the arrest, the line *ad* gives the duration of the arrest for the case that the thermometer measures essentially the temperature of the crystallization boundary.

The duration of the arrest is proportional to the heat of fusion *R* and inversely proportional to the rate of cooling $\frac{dT}{dz}$. On the basis of the duration of the arrest the heats of fusion and transformation can be approximately determined. If the cooling curve is determined for a substance with unknown heat of fusion *R_x* and under the same conditions the cooling curve of a substance with known heat of fusion *r*, then

$$R_x = r \frac{(ad)_x \left(\frac{dT}{dz} \right)_x}{(ad) \frac{dT}{dz}}$$

Here (ad) and (ad)_x designate the duration of the arrest and $\frac{dT}{dz}$ and $\left(\frac{dT}{dz} \right)_x$ the rates of cooling at the temperatures of the two arrests before the beginning of crystallization.

In this way the amount of the heat of fusion can also be compared with the heat of transformation. If we refer the magnitude designated by the index *x* to the transition point and the other magnitude to the melting point, we easily obtain the ratio of the heat of fusion to the transition heat. As a rule the transition heat is much smaller than the heat of fusion; with metals this relation always holds. With salts, however, exceptions occur. The heat of fusion for Li2SO4 is only 1/6 of the heat of transition, for Na2SO4 it is 0.58 of the heat of transition (*Z. anorg. Chem.* 43, 219 (1905)), for K2SO4 it is 3.5 times the transition heat and for Rb2SO4 it is 22 times the heat of transition.

Also cases are known where, when *p* = 1 kg., the heats of transition are vanishingly small since in the neighborhood of this pressure the neutral curve, i.e., where the heat of transition goes through the zero value, intersects the transition curve. The transition heat of K2Cr2O7 with a very large volume change is extraordinarily small, and in the transformation of α—β nickel the volume change as well as the heat

of transition are extraordinarily small. Finally the transition of Ice I' into Ice III' goes through the 0 value at -43° and 2200 kg. per sq. cm. while the volume change is about 16% of the volume of ordinary ice. (*Kristallisieren und Schmelzen*, p. 332.)

3. Specific Volume.

The relation of the volume to the temperature at constant pressure is represented by a line similar to the heat content (Fig. 16). If the heat content Q in this figure is replaced with $V - V_T = 0$ and the heat fusion R_p with the volume change Δv on melting, the diagram represents the relation of the volume to the temperature at constant pressure. The expansion of the substance $\frac{d_p v}{dT}$ like the specific heat c_p above -100° increases only slightly with the temperature in the crystalline and liquid state. If the critical point is not too closely approached, the relation of the expansion $\frac{d_p v}{dT}$ in the gaseous, liquid, and anisotropic state is

$$\frac{d_p v}{dT} > \frac{d_p v'}{dT} > \frac{d_p v''}{dT}$$

At the melting point the two lines f and k (Fig. 16) which represent the relation of the volume to the temperature, have a direction so that by the linear prolongation they intersect at $T = 0$. The following relation accordingly holds.

$$\left(\frac{d_p v'}{dT} - \frac{d_p v''}{dT} \right) = \frac{\Delta v}{T_s}$$

This relation is much better fulfilled than the analogous relation for the heat content, and exceptions to it are relatively rare. (H. Block, *Z. physik. Chem.* 78, 385 (1911).)

Rules analogous to those of Dulong and Petit and of Neumann-Kopp do not hold for the expansion with heat, and a rule analogous to the Crompton-Walden rule for volume change on melting holds even less.

Similarly to the discontinuous changes in the heat content on melting and transformation for anisotropic bodies the corresponding discontinuous change in volume may be used for determining the melting and transition temperatures. For this purpose the substance under investigation is placed in a dilatometer, the remaining space is then filled with an auxiliary liquid which does not act on the substance to be investigated and the observed volume plotted in relation to the temperature. At the temperature at which transition or melting takes place, there is a discontinuous volume change. Their amount can, however, be determined accurately only with elaborate precautions.

At high temperatures this process cannot be used since a suitable auxiliary liquid is not available. Under such conditions the relations of the length of a piece of the material to the temperature is determined to fix the volume change at the transition temperature. If the substance being investigated is quasi-isotropic as regards its volume change, this method is valueless.

For the determination of volume change on melting of substances having high melting points the procedure of Barus (*Phil. Mag.* V, 35, 173 (1893)) may be used. The substance to be investigated is placed in a narrow refractory tube of about 10 cm. length, and for a fixed position of the tube the position of the liquid meniscus is determined at the melting point by means of a micrometer screw and electrical contacts, then the substance is slowly crystallized from the lower end of the tube and finally the position of the meniscus again determined. The difference between these two positions multiplied by the average diameter of the tube, divided by the specific gravity gives the volume change on melting.

TABLE I
VOLUME CHANGE IN C.C. PER GRAM ON MELTING

Na	K	Rb	Cs
0.027	0.030 extr.	0.014	0.0139
	Zn	Cd	Hg
	0.010	0.0064	0.00259
Al	Ga	—	Tl
0.019	— 0.0053		0.0027
Si		Sn	Pb
<0		0.0039	0.0034
P		Sb	Bi
0.019		0.0022	— 0.0035
S	Se	Te	
0.029	0.018	0.012	
Cl	Br	I	
—	0.051	0.043	

The volume change in metals, at least so far as its sign is concerned, was early recognized by noting whether solid pieces sunk or floated in their melt. On account of deficient wetting, however, pieces of metals that do not expand on melting frequently do not sink. From this we may deduce a volume change which is not correct in its sign. As such an observation may be recalled the one that iron contracts on melting. The blow hole formation on pouring of iron with more or less carbon shows that iron obviously crystallizes with considerable volume decrease.

By volume decrease on crystallization rifts and cavities are easily formed between the crystallites. By crystallization under high hydrostatic pressure dense conglomerates without these cavities are obtained.

The volume on melting or polymorphic change, however, does not

necessarily change discontinuously. Along the neutral curves such a change does not take place, although the expansion with heat does change discontinuously along these curves. The volume isobar at the pressure of the maximum melting point is accordingly represented by two slightly curved lines that intersect at the temperature of the maximum melting point. This volume isobar accordingly lacks the discontinuous volume change on melting.

In a natural group the volume change on melting decreases with increasing atomic weight according to M. Toepler. (*Wied. Ann.* 53, 343 (1894).)



FIG. 19

For the natural groups in the narrow sense this rule appears to hold without exception.

Since a discontinuous change of volume takes place on crystallization, as a rule a volume decrease, the space which was occupied with liquid metal is not completely occupied by the metal after crystallization and consequently a pipe is formed in the metal ingot (Fig. 19). This pipe formation is a result of the volume change on crystallization; it occurs in the upper part of a cylindrical casting since because of the convection of the liquid, the cooler part of the liquid sinks and crystallization begins from underneath and from the walls. The liquid metal is forced by gravity between the crystallites or dendrites and runs to the upper part of the mold.

If the liquid metal entering the mold is heated only slightly above its melting point, pipe formation can only take place in cylindrical castings with metals which crystallize with decreased volume. How-

ever, with considerable overheating and complex mold form metals which crystallize with increase in volume may also form pipes. With a substance such as Bi or Si which crystallizes with an increase of volume, a globule is pressed out of the central part of the surface of a crystallizing cylinder. This phenomenon is not observed with metals which crystallize with a decrease of volume.

In practice we combat large and uneconomic pipe formation,

1. By casting the liquid metal in a high pressure cylinder and pressing the crystallizing melt.

2. By increasing the temperature of the upper part of the mold with its contents to keep the metal liquid here as long as possible.

3. By using a false top on the mold. Since pipe forms at the place where the melt crystallizes last, this place is kept outside the casting and in this case it takes place in the false top. During the crystallization the liquid metal from the false top must drain into all parts of the mold, if this condition is not fulfilled cavities are still formed in places where the metal from the false top cannot flow in.

4. Electrical Conductivity.

The resistance of a cube of 1 centimeter on each side, measured in ohms, is the specific resistance σ and the reciprocal of this value is the specific conductivity κ .

TABLE 2¹

He 0	Li 11.9	Be	B	C ² 0.034	N 0	O 0	F 0			
Ne 0	Na 21.1	Mg 24.0	Al 37	Si	P	S 0	Cl 0			
Ar 0	K 15.0	Ca 9.5	Sc	Ti 0.28	V	Cr	Nr	Fe 11.5	Ni 14.4	Co 11
	Cu 64	Zn 17.5	Ga 1.9	Ge	As 2.86	Se	Br 0			
Kr 0	Rb 7.8	Sr 4.0	V	Zi	Nb 5.4	Mo 17		Ru	Rh 18	Pt 10.0
	Ag 67	Cd 14.6	In 11.9	In 9.8	Sb 2.6	Te	I			
Xe 0	Cs 5.2	Ba	La	Ce	Ta 6.8	W 20		As 10	Ir 20	Pt 9.9
	Au 47	Hg ³ 4.5	Te 5.6	Pt 5.1	Bi 0.9					
		Ra		Th		U				

¹ K. Baedeker, *Die Elektrische Erscheinungen in Metallischen Leitern*, p. 21 (1910).

² Graphite.

³ Solid at -40° .

The preceding table gives a résumé of the conductivity of the elements at 0° expressed in reciprocal ohms $\times 10^{-4}$.

In a single natural group in the narrow sense, e.g.

K,Rb,Cs—Zn,Cd,Hg—(Ge),Sn,Pb—As,Sb,Bi

the conductivity decreases with increasing atomic weight. In the group Cu, Ag, Au the conductivity of silver is an exception. In the iron group and the platinum metals there is no relation between the conductivity and the chemical relations of the elements.

The relation of the conductivity κ of metals to the temperature is depicted in Fig. 20. With increasing temperature the metallic conductivity increases at ordinary temperatures practically linearly. At low temperatures, however, it increases rapidly so that the conductivity of silver at -260° is about 50 times as great as at 0° . At ordi-

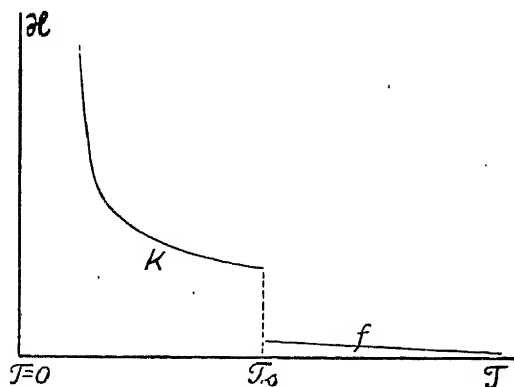


FIG. 20

nary temperatures the relative decrease for 1° C. is approximately equal to the coefficient of expansion of a gas. At the melting point T_s there is a large discontinuous decrease of the conductivity except with Sb and Bi.

The conductivity decreases with increasing temperature in the liquid state approximately as in the solid state. Therefore at about 1000° above the melting point the conductivity would disappear by linear decrease. The metals with high melting points are accordingly poor conductors in the liquid state. By passing to the vapor state the conductivity decreases extraordinarily, if we may judge from analogy to mercury. Since the metallic conductivity decreases on melting which takes place with increase in volume, it is to be expected that it would increase by increasing the hydrostatic pressure; this is found to be a fact. On the other hand, by elongating a wire, a decrease of conductivity should take place, which, so long as the elastic limit is not

exceeded, is equal to action of the hydrostatic pressure, but which has the opposite sign. The measurements of H. Tomlinson, E. Lisell and Beckman fulfill these expectations. (H. Tomlinson, *Proc. Roy. Soc., London*, 37, 386 (1885). E. Lisell, *Diss. Upsala* (1902), and B. Beckman, *Arsskrift Upsala* (1911).)

TABLE 3

E. LISELL		H. TOMLINSON	
Action of hydrostatic pressure.		Action of tension.	
Per cent. change of conductivity per 1 Kg./sq. cm.		Per cent. change of conductivity per 1 Kg./sq. cm.	
Pb	14.4×10^{-6}	Pb	-17.3×10^{-6}
Zn	6.1	Zn	- 4.4
Ag	3.5	Ag	- 4.2
Cu	1.8	Cu	- 2.3
Pt	1.8	Pt	- 2.3
Ni	1.4		

Concerning the change of resistance at very low temperatures extensive experiments have been carried out by Kammerlingh Onnes (*Comm. Phys., Lab. Leiden*, 129, 132, a and b, 133, etc.) and his co-workers. The resistance of a mercury wire decreases discon-

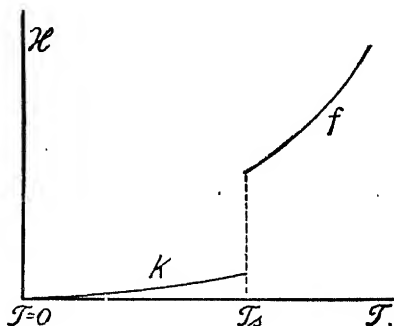


FIG. 21

tinuously on cooling below $T = 4.2^\circ$ to a vanishingly small value at least 10^{10} times smaller than that at $T = 273^\circ$. With Sn the temperature of the discontinuous decrease of the resistance is $T = 3.5^\circ$ and with lead at $T = 6^\circ$. K. Onnes calls these metals below the sharp decrease in resistance superconductors, since in this state they show an entirely characteristic electromagnetic behavior. The discontinuous decrease of the resistance is indicative of the occurrence of a new phase. However, the specific heat changes at the breaking point of the resistance in a normal way and what is especially remarkable is that the heat conductivity which usually is closely associated with the electrical conductivity changes continuously.

The electrolytic conductivity κ differs from the metallic by a reverse relation to the temperature, Fig. 21. At low temperatures the electrolytic conductivity is vanishingly small; it has, however, quite appreciable value near the melting point T_s if this, as with salts, is at high temperature. At the melting point the conductivity of a salt increases very greatly and discontinuously and increases further with increasing temperature. (R. Lorenz, *Elektrolyse geschmolzener Salze* II, p. 199 (1905).)

The electrolytic conductivity depends on the number of ions in a unit of volume and the frictional resistance that they encounter in wandering. If the number of ions increases with increasing temperature an increase of conductivity with increasing temperature is to be expected. At the temperature of the boiling point the conductivity decreases very greatly, since the number of ions in a unit of volume becomes very small.

The sulfides of the heavy metals and certain oxides have an astonishingly good conductivity even at low temperatures and indeed these substances conduct metallically. With magnetite (Koenigsberger, *Ann. Physik.*, 32, 179 (1910)) Fe_3O_4 the conductivity decreases with increasing temperature at first, reaches a minimum at 220° and then increases rapidly. Below 220° the temperature relation of the conductivity accordingly indicates metallic conduction; above 220° , however, the electrolytic conduction appears to exceed the metallic. These conclusions appear probable, although above 220° the polarization which is characteristic of electrolytic conduction is not observed; however, at high temperatures there is considerable difficulty in detecting the polarization since strongly depolarizing actions occur as is demonstrated by the glow of the Nernst lamp (Bose, *Ann. Physik.* (4), 9, 164 (1902)). Since the melting point is characterized by a discontinuous change of the conductivity, metallic as well as electrolytic, such a change should also appear at the transition point. This coincides with the facts for a series of transition points of metallic substances and also for electrolytically conducting bodies: AgI according to W. Kohlrausch at 145° (*Wied. Ann.* 17, 642 (1882)); Ag_2S at 175° and Ag_2Se at 133° according to Baedeker. While with AgI and Ag_2S the conductivity on exceeding the transition point increases greatly with increasing temperature, it falls with Ag_2Se .

At the transition points of Si, Ti and Tl, a discontinuous change of the conductivity appears. With iron, according to LeChatelier, the change of the conductivity at the lowest transition point is not discontinuous as one would expect for a pure metal but is a continuous one. Morris (*Phil. Mag.* (5), 44, 232 (1897)) and Harrison (*Phil. Mag.* (6), 3, 192 (1902)) found that the resistance of iron between 760° - 900° increases faster than at lower or higher temperatures but that this increase is continuous and that the two transition points of Osmond at 760° and 880° are not characterized by discontinuities in the curve of the electrical resistance.

Transition points may be indicated in the conductivity-temperature curves only by a change of direction where there is a different relation of the conductivity to the temperature for the two crystals but no difference in conductivity at the transition point itself. Such inflections are found for Ni, Sn, and Zn at 350°, 161°, and about 300° respectively. Naturally every inflection in the curve for the temperature relation of the conductivity is not to be considered as establishing a transition point; since especially with large grained metals, such as zinc, the release of strains by temperature changes may easily form or close gaps between the crystallites and thereby cause an inflection. The variability of the temperature relation of the conductivity as indicated by an inflection in the curve in the conductivity must accordingly be checked by the appearance of a discontinuous change of volume or heat content at the same temperature.

With Ni, Sn, and Zn at the above temperatures, besides the inflection in the curve for the conductivity, discontinuous changes are observed in the volume or heat content and it is thereby established that we are dealing with a transition point at which the expected discontinuous change of the conductivity is so small that it escapes observation. (M. Werner, *Z. anorg. Chem.* 83, 275 (1913).)

5. The Magnetic Properties of Metals.

Metallic bodies may either concentrate or disperse the magnetic lines of force; bodies in which the lines of force are concentrated are designated as paramagnetic, those which disperse them as diamagnetic. Under paramagnetic substances the ferromagnetic are characterized by a high capability of concentrating the lines of force. Besides this the ferromagnetic substances are distinguished from the non-ferromagnetic by another condition. With ferromagnetic substances the susceptibility κ depends on the field strength, and is greatly decreased by large field strengths. With non-ferromagnetic substances, with weak para and with diamagnetic substances, κ is independent of the field strength. If with such substances κ decreases with increasing field strength one is justified in concluding that ferromagnetic impurities, especially iron or its compounds, are present. Non-ferromagnetic substances are however known in which the susceptibility decreases with increasing field strength.

If we designate with \mathfrak{I} the intensity of magnetization per unit of volume due to a field of strength κ the susceptibility κ is determined by the relation $\frac{\mathfrak{I}}{\kappa}$.

With the ferromagnetic metals Fe, Co and Ni, \mathfrak{I} is practically independent of the temperature for a constant field strength as is also κ . Only a small decrease of \mathfrak{I} is noticeable with increasing temperature; however, \mathfrak{I} decreases discontinuously at a definite characteristic temperature for each metal.

In Fig. 22 the relation of \mathfrak{J} at constant field strength to the temperature is plotted. With all three ferromagnetic metals the intensity of magnetization, which at low temperatures is nearly independent of the temperature, falls at a definite temperature practically to zero. This takes place with nickel at 350° , with iron at 769° and with cobalt at 1100° . Only a very small amount of the magnetization remains which with increasing temperature disappears. The slow falling of \mathfrak{J} before its practically complete disappearance can be traced to the presence of impurities which, without exception, lower the temperature of disappearance of magnetism. To explain the small remainder of \mathfrak{J} which remains above the temperature of its practically complete disappearance it must be assumed that a small part of the ferromagnetic

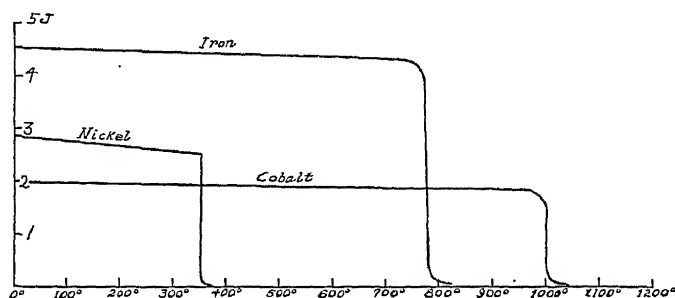


FIG. 22

atoms go over to the space lattice of the crystal form built of non-ferromagnetic atoms. If with decreasing temperature the ferromagnetism reappears the same relations again appear, it is at first very weakly magnetic, then it suddenly appears stronger and reaches its high value again only after considerable temperature lowering.

For the non-ferromagnetic elements K. Honda has determined the susceptibility χ and divided it by the density at room temperature. The susceptibility so reduced to equal volumes at room temperature is designated χ and plotted in relation to the temperature in figures 23, 24, 25, taken from Honda. (*Ann. Physik.*, 32, 1057 (1910).)

With diamond, B, Mo, W and Os χ is independent or nearly independent of the temperature up to 1100° . The curves for Mg, Ru and Mn show that these metals had a certain iron content since χ shows a strong decrease in the neighborhood of the transition temperature of iron, and further decreases with increasing field strength. It is seen that at the melting point of P, Bi, Ag, Tl, Au, Pb, Te, Sb and Sn discontinuous changes of χ are noted. Breaks in the χ -curves occur at the melting points of Al, I, Na and Cd. No indications of melting are found in the χ -curves of Mg, Se, Zn, S, K and In.

If no discontinuous change of χ be found at the melting point, it

still ought to be present on curves representing χ referred to the volume at corresponding temperatures (not room temperatures). A discontinuous change of χ then appears which represents the relative volume change on melting. In all these cases the specific susceptibility

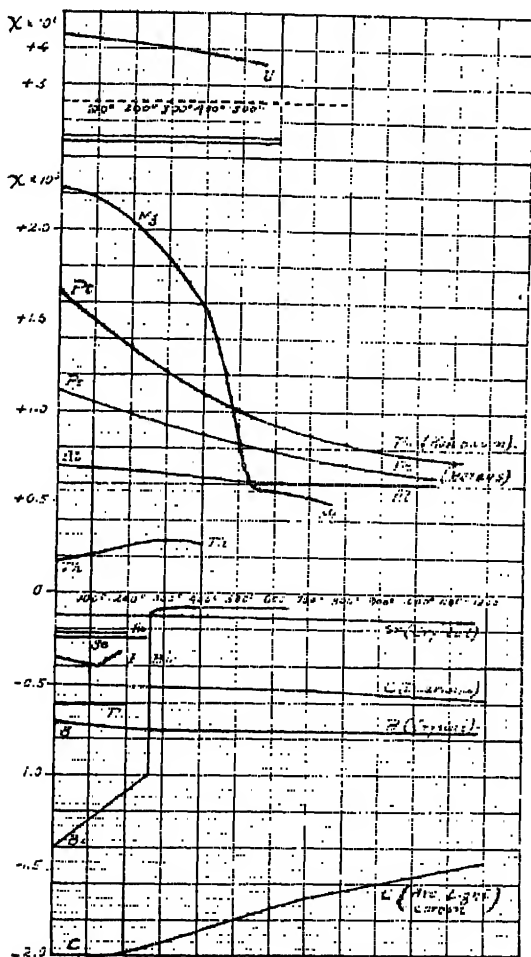


FIG. 23

reduced to the correct volume does not change discontinuously from the isotropic to the anisotropic molecule but merely as a result of the volume change. This is in any case approximated by the substances we have considered in which Honda's measurements show no discontinuous change of χ on melting. For a substance, however,

which shows a discontinuous change on melting there is, besides the influence of the volume change, still a large influence of the anisotropy of the molecules. With tin the anisotropic molecule is paramagnetic, the isotropic diamagnetic.

The transition point of thallium at about 230° may be recognized

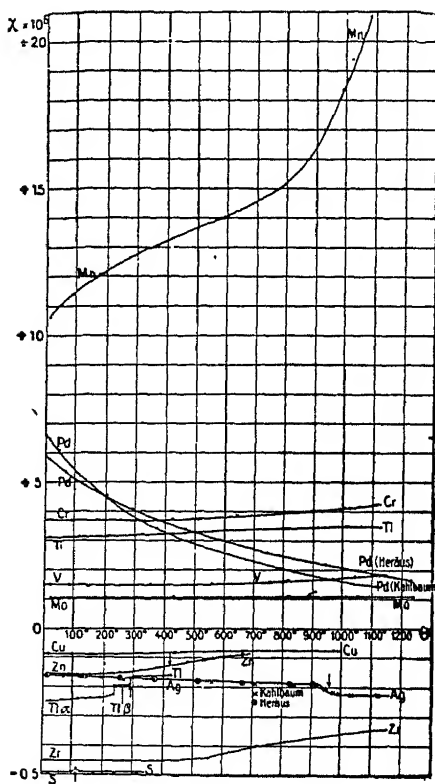


FIG. 24

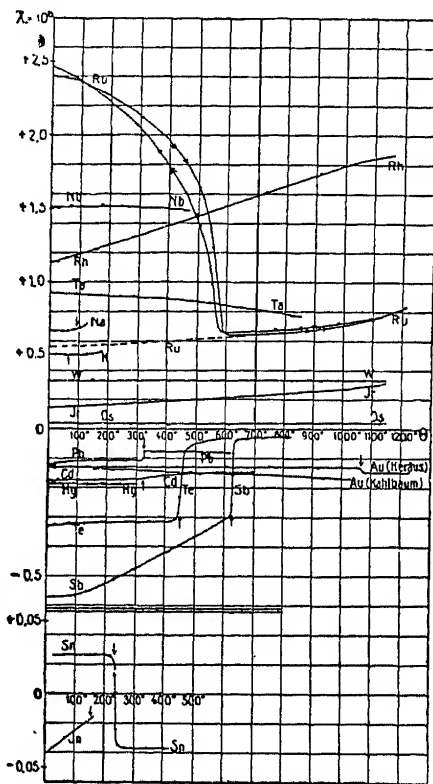


FIG. 25

by a discontinuity in the χ -curve. At the transition point of zinc at 300° a break in the χ -curve is present while the melting point of Zn is not recognized on the χ -curve. Finally the transition point of tin at 161° , the two transition points of Si at 210° and 440° as well as the transition point of Ti at 310° may be recognized from the χ curves.

6. The Solubility of Gases in Metals.

A. Sieverts (*Z. f. phys. Chem.* 60, 129 (1907); 74, 277 (1910); 77, 591 (1911); *Ber. d. d. chem. Ges.* 43, 893 (1910)) has determined the

solubility of hydrogen at constant pressure as related to the temperature for Cu, Ni, Fe and Pd and also the variation of the solubility at constant pressure with the temperature. At constant temperature the amount of dissolved hydrogen is not proportional to the pressure but to the square root of the pressure. The amount of gas dissolved at 760 mm. pressure increases as a rule with rising temperature. In Fig. 26 the ordinates rep-

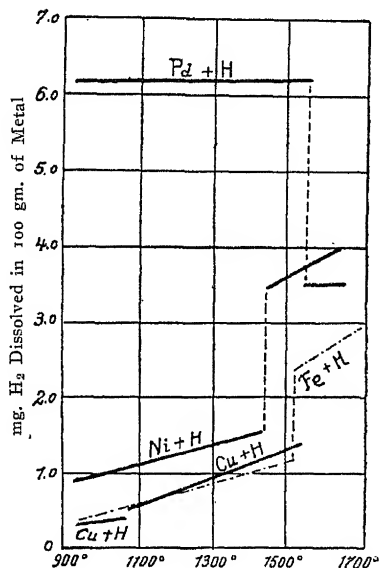


FIG. 26

resent the amount of hydrogen in milligrams per 100 grams of metal, while the abscissa axis is temperature. At the melting point of Cu, Fe and especially Ni the solubility of the hydrogen increases discontinuously. With iron a rapid increase of the solubility of hydrogen takes place between 850° and 900°, which increase within the limits of experimental error corresponds to the transition point of $\beta \rightleftharpoons \gamma$ iron found by Osmond at 880°. The transition point at 770° appears to correspond to no irregularity in the solubility curve. On the basis of the observations of Sieverts (*Z. physik. Chem.* 77, 597 (1911)) a sudden but small increase in the solubility of hydrogen in iron at 270° may be established. In the neighborhood of the transition point of nickel at 350° there are few observations, but a small discontinuous increase of the solubility here may not be excluded. If the phase of the solvent medium is changed by exceeding an equilibrium curve the difference of the molecular structure of the two phases accordingly corresponds to a different solubility of a foreign substance at the equilibrium temperature. Hence a discontinuous change of the

molecular structure of the solvent medium corresponds to a discontinuous change of the solubility.

7. The Temper Colors of Metals.

As is well known metals heated in air develop temper colors (*Z. anorg. Chem.* **111**, 78 (1920)). The series of these colors is in general that which is shown by layers of air of increasing thickness. The metals become covered with a thin layer of oxide whose rate of increase of thickness may be determined from the change of the temper color with time. Temper colors are formed on Ag, Cu and Pb at ordinary temperatures in iodine vapor. The rate of thickening of layers of AgI and PbI₂ may be easily followed. If the concentration of the iodine vapor is held constant by leading air containing a definite amount of iodine over a silver plate, the rate of thickness increase of the AgI layer $\frac{dy}{dt}$ is inversely proportional to the thickness y of the AgI layer already present.

$$\frac{dy}{dt} = \frac{p}{y} \quad (1)$$

Accordingly the following relation between y and t holds

$$y^2 = 2pt. \quad (2)$$

The thickness of the AgI layer lies theoretically on the positive branch of a parabola whose vertex is coincident with the origin of the yt coordinates and whose symmetry axis is the t axis.

This also proves experimentally correct. If the color of the silver plate in the iodine containing air stream is observed from minute to minute we can get on the basis of these observations the thickness of an air layer which would show the same color. If these thicknesses are divided (Landolt's Tables 1905, tab. 186, p. 610) by the index of refraction of AgI 2.27, we obtain the thicknesses of the AgI layer given in the following table.

Time in Minutes	Color	Thickness of Air Layer in $\mu\mu$	Thickness of the AgI Layer in $\mu\mu$	
			Found	Calculated
1.....	indigo	282	124	125
2.....	yellow green	409	178	176
3.....	red	490	216	216
4.....	blue	570	247	249
5.....	green	650	286	279
6.....	yellow green	680	299	305
7.....	pale yellow	720	319	330
8.....	dull purple	780	335	353
9.....	sea green	870	383	374
12.....	gray red	996	440	432
14.....	blue green	1160	515	489
17.....	flesh red	1264	554	514
21.....	blue green	1450	638	571

If we calculate the thickness of the AgI layers for the times given in the table, putting $2p = 155.5 \times 10^{-10}$ mm. the values given in the column "calculated" are obtained. From these it is evident that the thickness of the AgI layer changes with time according to the above parabolic equation.

The parabolic increase of thickness of the temper layer in relation to the time holds only for the action of Cl_2 , Br_2 or I_2 , on Ag, Cu and Pb and for the action of H_2S on Cu. The coloring of metals in air as a result of the formation of oxide layers, takes place according to another law. (W. Köster and Tammann, *Z. anorg. u. allg. Chem.* 123, 196 (1922).) This law may be expressed,

$$t = ae^{by} - a \quad (3)$$

and

$$\frac{dy}{dt} = \frac{1}{ab} e^{-by}. \quad (4)$$

In these equations a is a constant independent of the temperature. The constant b determines the retardation of the thickness increase

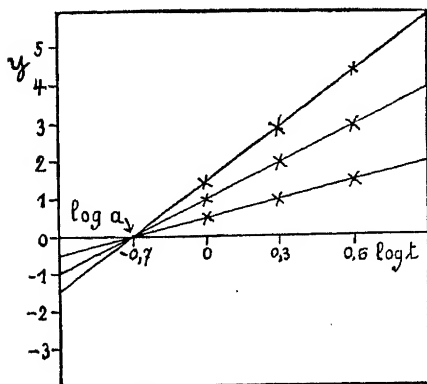


Fig. 27

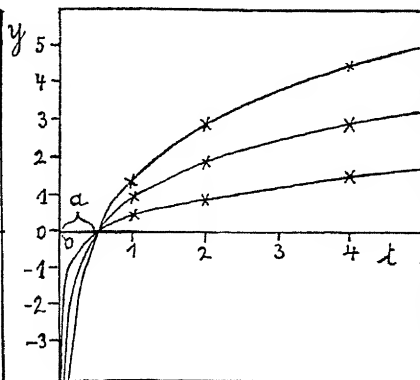


Fig. 28

of the outside layer with increasing time t and has an exponential relation to the temperature. For the start of the reaction the initial velocity is

$$\frac{dy}{dt} = \frac{1}{ab} \quad (5)$$

The geometrical meaning of a is the following. If we plot the logarithm of t as abscissae and the values of y as ordinates we obtain a line for every temperature all of which intersect the $\log t$ axis at the value $\log a$ (Fig. 27). If on the other hand the value t is plotted as abscissae and an exponential curve is obtained for every temperature

these curves intersect in a point. The distance of this point from the origin of the coördinate system is a . In Fig. 27 the value of $\log t$ corresponds to the values of t in Fig. 28 and the values of y are the same in both.

From equation (3) we get

$$b = \frac{\ln(t + a) - \ln a}{y} \quad (6)$$

b is accordingly the tangent of the angle at which the line in Fig. 27 cuts the y axis.

Since a is independent of the temperature and b is an exponential function of the temperature it follows

$$b_T = b_{T_0} e^{-c(T - T_0)} \quad (7)$$

The two laws indicate nothing further about the velocity of the chemical reaction causing the temper color than that it is very large. For the rate of thickness increase it follows from the first law that at the first moment it is infinitely large and from the second law that if it is not infinitely large it is very great in comparison to the velocity of diffusion of the reagent through the layer of reaction product, since in equation (5) a and b are real fractions.

TABLE 4

Metal	Years	Initial Velocity $\mu\mu$ per minute	Seconds
Pb	90	219	0.42
Zn	$31 \cdot 10^2$	104	0.88
Cd	$19 \cdot 10^5$	778	0.13
Cu	$6 \cdot 10^8$	89	1.11
Sn	$36 \cdot 10^8$	856	0.15
Fe	$25 \cdot 10^{17}$	2712	0.05
Ni	$475 \cdot 10^{17}$	146	0.95

Fig. 29 refers to the tempering of iron in air. The thickness of air layers corresponding to the temper colors are plotted against $\log t$. The temperatures at which the tempering took place are shown on the lines. These lines intersect the $\log t$ axis at 0.001 minute. a is accordingly independent of the temperature and b is the tangent of the angle at which a given line intersects the y axis. The relation of b to the temperature is given by: $b = 4.4e^{-0.00867(T - 280 + 273)}$.

The thickness increase of the oxide layer on metals is greatly retarded since the oxygen concentration is diminished from layer to layer. The value of b can accordingly be considered as a coefficient of decrease of oxygen concentration.

The course of oxide layer formation at low temperatures can be derived from that at high temperatures by means of the equations given. In the preceding table the times in years are calculated for the first visible coloring of various metals in dry air at 15° . This first yellow corresponds to an air layer 164μ thick which divided by the index of refraction of the oxide gives the thickness of oxide layer corresponding to the first yellow.

The initial velocities in μ per minute $\left(\frac{1}{ab}\right)$ for 15° are also given in the table. If the action of the oxygen were not hindered by the

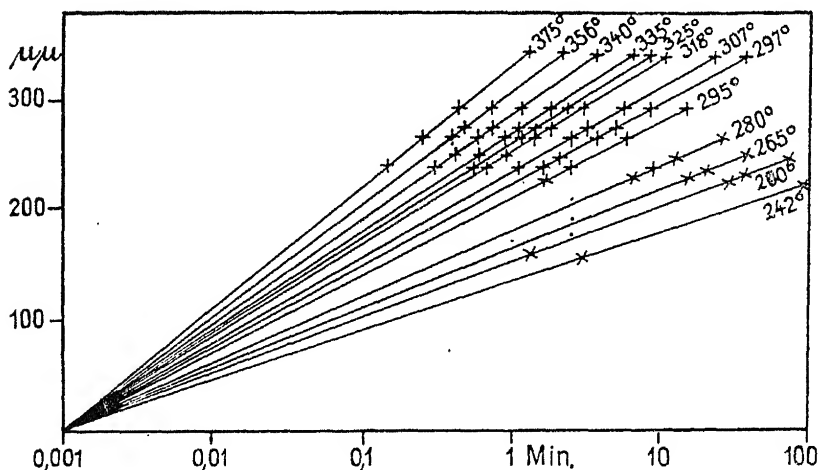


FIG. 29

oxide layer iron would have passed through all visible temper colors in one minute while with copper only the first yellow would be reached after one minute. Despite these high original velocities it requires a very long time to reach the first yellow at 15° .

In the third column the time in seconds is given which corresponds to an air layer 14.10^{-7} mm. This time approximately corresponds to the formation of the first lattice plane of the oxide.

From the experiments at higher temperatures it follows that metals are practically instantly covered with an oxide layer which even if it is very thin protects the metal from oxidation so well that further oxidation is inappreciable. In dry air the metals remain many years without showing temper colors.

In damp air the change of the metals proceeds much more rapidly and dry oxidation is not to be confused with moist.

The position and inclination of the lines in Fig. 29 are independent of the oxygen content of the O_2 - N_2 mixture from 0.5% to 100% O_2 .

In pure oxygen the inclination of the lines change when the pressure is less than 2 mm., the a value increasing and the b value decreasing. (E. Schroder, *Z. anorg. Chem.* 127 (1923).)

From this it may be concluded that an adsorbed oxygen layer forms over the oxide layer. This is confirmed by the relation of the value $\frac{I}{a}$ to the pressure which is the same as that for the relation of the amount of gas absorbed on charcoal to the pressure.

With Fe and Ni the nature of the oxide layer does not change and at various temperatures the same oxide is formed. Hence, $\log b$ is a linear function of the temperature. The increase in thickness on the tarnishing of cerium and lanthanum in O_2 or N_2 takes place on broken logarithmic lines. Each part of such a line corresponds to a different kind of oxide. It is not probable that these kinds differ in their chemical composition. More likely they are different forms of the same substance.

Also the tarnishing of Cu takes place along broken logarithmic lines and each succeeding part is steeper than the one before. At low oxygen pressures the broken line consists of 3 or 4 parts while at higher pressures the line is only broken once. The second of the parts at low pressures is much flatter than the third and fourth parts. As a result of this there is after a time a more rapid increase in thickness of the oxide layer at low pressure than at high, not because oxygen at low pressures oxidizes the copper more rapidly than at high pressures but because at low pressures the oxide layer formed is more permeable to O_2 .

The colors that develop on quenched steel by tempering serve to differentiate the degree of tempering. These colors depend principally on the furnace temperature and time of heating and therefore on the mass and form of the piece to be heated; they are independent of the O_2 content of the furnace.

The development of temper colors is a means of making visible the microstructure of iron alloys. With increasing Ni content the thickness increase of the temper layer is delayed (Meteoric Iron). Cementite colors more slowly than ferrite and iron phosphide still more slowly. Even the individual ferrite grains color with different velocities. The color on any one grain is the same but the different grains may be distinguished.

The cycle of temper colors formed at the same oxygen concentration is determined by the diffusion coefficient of the oxygen into the oxide layer. This should be the same in an isotropic oxide layer on all ferrite grains and all ferrite grains would therefore be colored the same. If however the oxide layer is anisotropic and its crystallographic orientation is determined by that of the ferrite grain on which it is deposited the diffusion coefficient of oxygen in the differently oriented oxide layers may be different and the result of this would be a different color on the differently oriented ferrite grains.

8. The Reactions of Metals with Electrolytes.

The position of the metals in the electromotive series is determinative of these reactions. The potential of a metal in contact with a solution of its salt is given by the following expression:

$$\frac{RT}{nF} \ln. \frac{P}{p}.$$

Here P is a characteristic constant of the metal, i.e. the solution pressure, p is the osmotic pressure of the ions of the metal in solution, R the gas constant, T the absolute temperature, n the valence with which the metal goes into solution and $F = 96500$ coulombs. With constant temperature the potential increases with increasing osmotic pressure of the ions, hence the potential of different metals is to be compared at the same osmotic pressure of their ions in the electrolyte, e.g. at $p = 22.4$ atm., i.e. at an ion concentration of 1 gram ion per liter at 0° .

If the metals are arranged according to the magnitude of their potentials in solutions which meet these conditions the following series is obtained. The kind of ion in which the metal goes into solution is given.

	Mg''	Zn''	Fe''	Cd''	Tl'	Co''	Ni''
Volt	—1.55	—0.76	—0.43	—0.40	—0.32	—0.29	—0.22
	Pb''	Sn''	H'	Cu''	Ag'	Hg''	Au'
Volt	—0.12	—0.10	0.00	+0.34	+0.80	+0.86	+1.5

The potential of a cell which consists of two metals in contact with their solutions which contain 1 mol ion per liter is given at once by subtraction of their potentials.

A metal only precipitates metals following it in series. Correspondingly hydrogen may be evolved from acids or water decomposed only by metals which precede hydrogen in the series. On the surface of a metal that is less noble than hydrogen, e.g. Fe, metals less noble than iron protect it from decomposing water. In a galvanic cell Zn-water-Fe the Zn goes into solution and the H_2 is adsorbed on the iron whereby it is protected from oxidation. On the other hand nobler metals than iron not only do not protect it but contribute to its destruction by rust formation. In the cell Fe-water-Sn the iron goes into solution and the tin is covered with H_2 . Since with galvanizing and tinning of iron sheet, places can always be found where water may come in contact with the Fe. For example, it is exposed to rain, the tinned sheet quickly becomes unsightly from rust formation while the galvanized sheet retains its original appearance for considerable time.

The solution velocity of base metals in acids may in general be easily measured by the hydrogen evolved in a short time. If we

designate the volume evolved per minute as $\frac{dx}{dt}$ the solution is proportional to the surface of the metal piece O and proportional to the acid concentration present at that moment.

Since at the beginning of the solution the acid concentration is the greatest, $\frac{dx}{dt}$ should have its greatest value at the start and decrease proportionally with the time. For non-metallic substances, e.g. marble, the velocity of CO_2 evolution is with constant surface inversely proportional to the time. But with metals, e.g. Zn, the solution proceeds at first with very low velocity, increases to a very outstanding maximum and then decreases as the acid concentration decreases. The abnormal increase of the reaction velocity (the induction time) may be explained by the assumption that as the solution starts the nobler impurities are segregated on the surface, whereby local cells result, in which the zinc goes into solution and the hydrogen is evolved from the electropositive impurities. This explanation due to de la Rive has been supported in many ways by Palmaer and Ericson-Aurén. (*Z. anorg. Chem.* 27, 209 (1901); *Z. physik. Chem.* 39, 1 (1902), 45, 182 (1903).)

9. Properties that do not Change Discontinuously During Melting or Transition.

Vapor pressure is a property of this group. At the melting point the vapor pressure curves of a crystal and its melt intersect, and at the transition point the vapor pressure curves of the two forms that are in equilibrium intersect. If at these equilibrium temperatures the vapor pressure changed discontinuously it would be obviously possible to construct a *perpetuum mobile*. In a U-tube (Fig. 30) we may have at constant temperature above a layer of crystalline substance k the vapor of pressure p and above the liquid f the vapor of pressure p_1 . If $p_1 > p$ it would be possible by opening or closing the cock b to move the piston a . Accordingly if the difference $p_1 - p$ were not a zero at the temperature of melting any quantity of work could be obtained. Since however the construction of a *perpetuum mobile* is from experience not possible it is obvious that $p = p_1$. Since, further, the relation of the vapor pressure to the temperature is different for the liquid and crystalline substance the two vapor pressure curves must intersect at the melting point. For the position of the vapor pressure curves of a substance in the liquid and crystal state at the intersection point the rule holds that the prolongation of the vapor pressure curve of the liquid must fall in the phase field of the crystal and the prolongation of the vapor pressure curve of the crystal must fall on the phase field of the liquid. (Fig. 31.) Since liquids frequently supercool (crystals may not be overheated

without melting) the same substance can be obtained in either the liquid or crystalline form at the same temperature beneath its melting point. The vapor pressure of the liquid is greater at the same temperature than that of the crystal, and the supercooled liquid has accordingly the tendency to distill to the crystals and condense in the crystalline state. The angle α at which the vapor pressure curves of a crystal and its melt intersect is smaller the less the difference of volume of the liquid and the crystal in comparison to the volume change on vaporization. Since the volume change on vaporization in comparison to that on melting is as a rule very great while the vapor pressure of the liquid and its crystals are very small at the melting

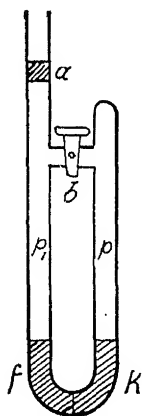


FIG. 30

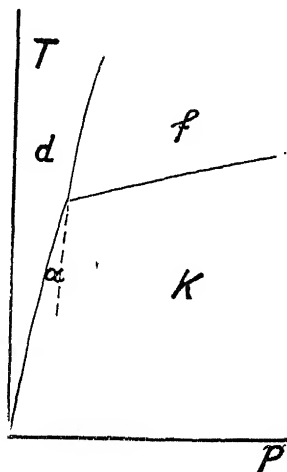


FIG. 31

point, the difference in the vapor pressure of the supercooled liquid and the crystals is exceedingly small and is according to very careful measurements the same for water (Juhlin, *Z. physik Chem.* 14, 187 (1894)), and benzol (Ferche, *Wied Ann.* 28, 440 (1886)).

For the osmotic pressure of a substance at its melting point a relation entirely analogous to that shown in Fig. 31 holds. The osmotic pressure of water dissolved in chloroform is the same whether the chloroform is in contact with liquid water or ice at the equilibrium temperature of ice and chloroform saturated water. At low temperatures the osmotic pressure of chloroform in contact with supercooled water is greater than that which is in equilibrium with ice at the same temperature. Further since the osmotic pressure increases with the concentration of the dissolved substance, the relations which hold for the osmotic pressure may be carried over to the solubility. If in Fig. 31 we replace p with the solubility l in relation to the temperature, we obtain two curves for ice and water

that intersect at the melting point of ice and below the melting point the solubility of the supercooled water is greater than that of the ice. On the other hand the solubility of chloroform in water is discontinuously decreased by the change into ice.

These relations for the vapor pressure hold over a still further range for the thermodynamic potential. If the forms (phases) of a chemically homogeneous substance have the same potential they are in equilibrium with each other. If we construct the surfaces of the thermodynamic potential over the p, t plane for the three states of a chemically homogeneous substance these surfaces intersect mutually above the equilibrium curves of vapor and liquid, liquid and crystal, vapor and crystal, crystal and crystal. Over the field of existence of the form that is stable in this field, the related surface for the potential is the lowest. (The thermodynamics of one component systems. *Ann. Physik.* 36, 1027 (1911).)

The electromotive force of a transition cell in relation to the temperature can always be represented by two curves which intersect at the transition point. Such a cell can be obtained (E. Cohen, *Z. physik. Chem.* 14, 53 (1894); E. Cohen and G. Bredig, *l.c.*, p. 535, and Van't Hoff, Cohen and Bredig, 16, 453 (1895)) by the combination of a saturated solution of a salt that has a transition point and an unsaturated solution of the same salt by means of two unpolarizable electrodes. The saturated solution must be in contact with the crystallized salt.

The curve of the electromotive force in relation to the temperature of a cell formed of two different metals and two separate electrolytes shows a break at the melting point of either or both metals. Such a break also occurs in the eventuality of a transition point of either or both metals.

The same holds for the curve of the electromotive force of a thermoelement, a break occurring for every melting or transition point. In such a case if the thermoforce of two metals A and B is measured in relation to the temperature and the metal B has a transition point, by exceeding the transition temperature in the wire of the metal B a part of it is transformed into the form stable at high temperatures. At the junction of the two forms in the B wire no thermoforce occurs since the two forms are in equilibrium. The thermoforce of the metal A against the two forms of the B wire will change, however, with the temperature according to two different equations. The two corresponding curves intersect at the transition point of B, whereby a break occurs in the curve for the relation of thermoforce to temperature.

10. Summary.

We may divide properties into two groups according to their changes with change of the state of aggregation. The properties of the first group: volume, heat content, electrical conductivity, magnetic sus-

ceptibility and the solubility of gases change, in general, discontinuously with the change in state of aggregation. This discontinuous change of properties is lacking only in singular points of the equilibrium curves of two different states of aggregation, i.e. the intersections of the neutral lines with the equilibrium curves.

As a rule the change of properties on melting is very much greater than that on the transition of a crystalline form. As exceptions to this rule are to be noted (*Krystallisieren und Schmelzen*, p. 339), the large volume change on the transition of ice I to ice III which exceeds the volume change on melting both kinds of ice, the large heat transition of Li_2SO_4 and Na_2SO_4 which exceed the corresponding heats of fusion, and the change of magnetic susceptibility of ferromagnetic metals.

The properties of the second group, the vapor pressure, the thermodynamic potential, and the electromotive force of transition cells do not change in a discontinuous way with the change of state of aggregation. If so, the construction of a perpetuum mobile would be possible.

If at the singular points of the equilibrium curve or on the neutral curves of the properties of the first group a discontinuous change does not take place on the transition of the substance there is a discontinuous change in the relation of these properties to the pressure or temperature since the property isotherms or isobars intersect at the equilibrium point with a large or small angle. The same also holds for the change of properties of the second group with temperature and pressure. If in the first derivative of a property of the second group a discontinuity does not occur at a point in the equilibrium curve one is to be expected for the second derivative.

In practice the fixing of transition points is done according to the following rules. 1. The measurement of the properties of the first group for the purpose of discovering the transition point, since this places less requirements on the exactness of measuring than the measurement of those of the second group. 2. If the isotherms or isobars of a property of the first group lack discontinuity on transition it will occur on the corresponding curves of the first derivative of the property, with regard to the pressure or the temperature.

C. The Changes of Properties by the Working of Metals

The following changes of their properties are to be observed in metals after permanent deformation. The elastic limit is increased extraordinarily and with copper may be brought to 14 times its value for the undeformed metal which results from crystallization of a melt. The elastic properties themselves, the modulus of elasticity, etc., are only relatively slightly changed. For the modulus of elasticity a

change of up to 20 per cent. is found. By a certain kind of working, wire drawing, the same order of magnitude of change can be attained for a second group of properties—the electrical conductivity and probably also the heat conductivity. Still the changes in the two groups of properties are not parallel. It is known with certainty that with very great deformation, as with wire drawing, the specific volume of some metals increases around 0.1 per cent. The energy content of a metal is also increased by working.

All these changes of properties may be reversed by heating the worked metal. The micro-structure of the cold worked metal changes with the properties. The original crystallites are divided up by glide planes and the parts displaced over one another. A fibrous structure that is especially conspicuous in cold drawn wire and cold rolled sheet results.

For the explanation of the very remarkable changes of properties of metallic bodies on permanent deformation three different conceptions have been developed.

The current explanation assumes the formation of a new modification of the metal by its permanent deformation. Since the change of properties increases with the degree of deformation, it is assumed that the amount of the new modification increases with the degree of deformation, and that through its presence the change in properties is brought about. Microscopically or by transmitted X-rays the formation of such a new modification cannot be demonstrated. A statement of this explanation has been put forward by Beilby (*Proc. Roy. Soc., London*, 76A, 462 (1905)) with the modification that by the deformation the space lattice of the crystallites is disorganized so that amorphous particles are formed whose amount increases with the degree of deformation. We will see, however, that the crystals possess directions of resistance that are preserved from becoming amorphous by deformation.

The modification hypothesis was set up at a time when nothing was known of the phase diagram of metals. At the present time one is cautious in assuming modifications (new phases).

A second viewpoint has recently been proposed by A. Smits. (*Z. physik. Chem.* 76, 444 (1911).) By pressure and temperature changes the molecular composition of a substance which consists of two molecular species may change. If now the change of the molecular composition is not reversible, a partial change may remain after a return to the original pressure and temperature. This would naturally cause a change in the properties by deformation. Since we are considering here a change in the internal composition, a change in the microscopic structure of the substance is not necessary. In general, a change of temperature of 1° will bring about the same change of the internal composition as a pressure change of 1000 atmospheres. Since, however, by large quick temperature changes of 100°-1000° a noticeable change in the properties of many metals is not brought about, it

is not permissible to trace back the property changes which are brought about by relatively small pressure changes to a change of the internal composition. Further, the action of a high hydrostatic pressure (up to 3000 km. per sq. cm.) in such a way that no permanent deformation of the compressed piece of metal remains produces no change of properties. The change of properties is bound up with the deformation of the metals, and the magnitude of the pressure change only comes into consideration insofar as it is necessary to attain the deformation. Finally, the recent investigations of atomic structure show that in metals the same kind of atoms oscillate around the lattice points, hence the assumption of different kinds of atoms required by Smits is not tenable.

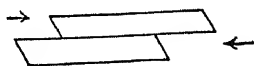


FIG. 32

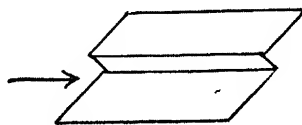


FIG. 33

A third explanation of the effect of cold working of metals on their properties has been worked out by the author on the basis of crystallographic facts. This theory is considered here with a series of data corresponding to the importance of the question.

The various views concerning the change of the properties by cold working have been recently collected in a monograph, "The hardening of metals by mechanical treatment," by W. Fraenkel, Berlin, Springer, 1920.

1. Crystallographic Basis.

Deformation of a crystal below the elastic limit is always homogenous deformation, i.e. points of equal distance in parallel lines remain at equal if changed distances and return after the deformation to the parallel lines. (W. Thomson and P. Tait, *Text-book of Math. Physics*.) If the deformation increases above the elastic limit the resulting deformation of a single crystal is likewise homogenous deformation. Therefore on one hand a displacement can take place such that the optical properties of the displaced part of the crystal are not changed relative to the remaining part. In this case the two parts of the crystal will only be displaced relative to one another (Fig. 32). On the other hand by the displacement in a lamella between the displaced and the remaining part a change in the optical orientation takes place; in this case a rotation as well as displacement takes place in the lamella, i.e. the lamella becomes a twinning lamella (Fig. 33). Both kinds of gliding may go on to a considerable extent without a break resulting. The first simpler kind of gliding discovered by O. Mügge is called Translation (O. Mügge, *N. Jahr. f. Min.*, 1895, II,

p. 211), the second complex kind of gliding discovered by E. Reusch is called "simple displacement" (E. Reusch, *Pogg. Ann.* 132, 441 (1867); 147, 307 (1872)).

By deformation gliding planes always occur in the crystallites of plastic metals and in greater number the more drastically the metal is deformed. It has long been known that many fine dark lines appear on a well-polished surface after deformation of a metal specimen which extend only to the boundaries of the crystallites in which



FIG. 34

Piece of soft iron after great deformation. $\times 300$

they occur. If a metal cube that is polished on one side is cautiously deformed in a vise by means of pressure parallel to the polished side dark lines vertical to the direction of pressure can be seen by microscopic observation at first only in a few crystallites. By increasing the pressure and accordingly the amount of deformation dark lines appear in still other crystals with always decreasing angle to the direction of pressure. These dark lines, the glide lines, represent the intersection of the glide planes with the plane of the section. Along the glide lines discontinuities, i.e. steps, are formed. These steps appear as dark lines by vertical illumination while the polished plane appears bright.¹

¹ In mechanics it is shown that by compressing a homogeneous cube it breaks apart along planes that go through the edges of the cube which are vertical to the direction of pressure. Along these planes the compressive strength has

With gold and copper there are formed by slight deformation first glide lines then the outlines of the crystallites which are inclined more or less to the plane of the section. In other metals this order is reversed and in some cases, as with Ag and Ni, they occur practically simultaneously. (O. Faust and G. Tammann, *Z. physik. Chem.* 75, 108 (1910).) Therefore, after drastic deformation all the crystallites cannot be simultaneously brought into sharp focus under the microscope. Fig. 34 shows the picture of the polished surface of a very soft piece of iron after drastic deformation, and Fig. 35 shows the picture of a polished surface of electrolytic copper after deformation. With iron, glide surfaces have formed in all crystallites and a part of the crystallites have been so greatly displaced that they appear dark

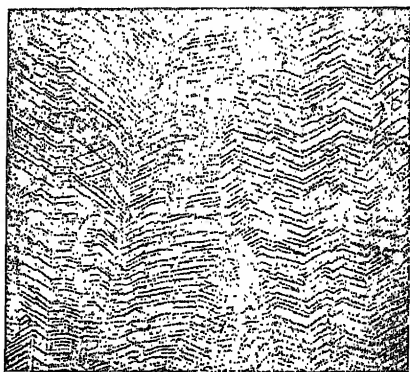


FIG. 35

Sliplines in electrolytic copper produced through tension exerted in direction of current. Direction of crystal growth top to bottom

since they cannot reflect light into the ocular. With electrolytic copper the deformation is much less evident and the long crystallites that are vertical to the electrode are hardly displaced with respect to each other. The first glide lines formed run vertical to the direction of pressure and stop at the boundary of two crystallites or change their direction at these boundaries.

We know only a little concerning the orientation of glide planes and the direction of displacement in metallic crystals. O. Mügge

a minimum value. The pressure per unit of surface P is in equilibrium with shearing strength of the material per unit of surface F . The following equation accordingly holds

$$P \cos \alpha = F \frac{1}{\sin \alpha} \quad \text{or} \quad P = F \frac{2}{\sin 2\alpha}$$

For $\alpha = 45^\circ$, P is a minimum. The first glide planes to occur, those whose glide lines are vertical to the direction of pressure, accordingly form an angle of 45° with the direction of pressure.

(N. Jahrb. f. Min. 1899, II, 54) found the glide planes (translation planes for Cu, Ag and Au crystals) parallel to the octahedral planes with a direction of displacement parallel to the edges of the octahedron, and with copper crystals also glide planes vertical to the octahedral planes. With α Fe the glide planes exhibit "simple displacement" parallel to the planes of the icositetrahedron. With cubic lead gliding takes place along the octahedral planes. The forces which bring about the glide planes parallel to and vertical to the octahedral planes in copper are different and the same holds for every further system of glide planes. By the most cautious deformation of single crystals the first glide plane system to appear is that for which the displacing force is the least. There are, therefore, still further glide plane systems of unknown orientation possible in the crystal under investigation. The more of such systems exist and the more numerous their directions of equal value the more plastic is the crystal. The direction of displacement also plays a part. The displacement along the glide plane is very little if the displacing force acts in a certain direction. The parts of a crystal separated by a glide plane are, therefore, not displaced with equal ease in all directions of the glide plane, and further there is a special property with respect to glide plane formation that may be designated as the ability for glide plane formation.

2. The Tendency to Form Glide Planes and Plasticity.

The preliminary conditions for the plasticity of a crystal may be formulated: (a) that the number of glide plane systems must be at least three, and (b) that the breaking strength of a crystal element bounded by three glide planes must be as great as possible in comparison to the force necessary for gliding. If these conditions are met the material will be plastic, i.e. it can be deformed by the application of sufficient force without breaking and will begin to flow if the applied force reaches a definite value.

Still the fulfilment of these conditions is not enough to explain the great differences in deformability of crystals of different substances, as calcite and gold, and also of the same substance at different temperatures. If the preliminary conditions are fulfilled the principal condition must still be met; namely, there must form, as soon as the deformation increases above the elastic limit, the greatest possible number of glide surfaces in the crystal, hence the greater the number of glide surfaces of the same system the more plastic is the crystal.

If two cubes cut from different crystals are acted upon by shearing moments of the same strength parallel to the direction of gliding, the resulting deformation can according to the nature of the substance be different by the formation of a different number of glide planes. In Fig. 36 the formation of a glide surface takes place by a four times greater displacement than the division of the cube as in Fig. 37 with the formation of four glide surfaces. The deformability is

accordingly determined by the number n of glide surfaces per unit length vertical to the direction of gliding. This number n changes in the same crystal with the glide plane system.

The number of glide planes is very much smaller than the number of layers of molecules. If they reached the number of the molecular layers, the grooves caused by the glide surfaces on the surface of a deformed crystal would be entirely imperceptible. There arises, therefore, the questions why the single molecular layers do not behave the same and why does not the deformation take place by the displacement of all the individual molecular layers over each other. Since the origin of a glide plane is an occurrence of very small probability, it can only occur if a series of conditions are fulfilled. By studying the ability of glide planes to form we may learn of these conditions.

The formation of glide planes protects a crystal from breaking on



FIG. 36

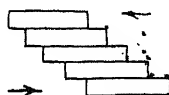


FIG. 37

drastic deformation. In the flow of crystals and crystal conglomerates the space lattice itself is preserved intact through the formation of glide planes, since the flow can only take place in directions determined by the glide planes. This is the essential difference between the flow of a viscous liquid and a crystalline conglomerate. While in a liquid the path of a particle, aside from the molecular motion, is a space curve, in a crystal conglomerate the path of a particle is a zigzag line which approaches a space curve more nearly the greater the number of glide plane systems and the greater the number of glide planes. Anisotropic and isotropic substances accordingly differ in their kind and method of flow.

It is worthy of note that in the formation of a twinning lamella, if the lamella is rotated by simple displacement (Fig. 33), it stops at the same angle of rotation. Those who have made these observations cannot agree with the conception that by thorough and complex deformation the inner structure of a crystal approaches the amorphous state.

The tendency to form glide planes n , the number of glide planes formed under a definite set of conditions, is a function of the temperature, the hydrostatic pressure, and the impurities present in the crystal.

The rate of flow of metal conglomerates through narrow openings depends on the friction at the glide surfaces, the number of their systems and the magnitude of n . If the relation of the friction to the temperature is known from special experiments, by comparison of

the changes of rate of flow and the friction with temperature and pressure a conception of the temperature and pressure relationship of n can be obtained.

The rate of flow of metals doubles with a temperature increase of 10° . The increase in rate of flow with the temperature is much more rapid in the case of other substances such as ice, phosphorous, etc. If we assume that the temperature relation of the rate of flow for metals is a result of the relation of the friction of the glide planes to the temperature, the number n for metals is independent of the temperature over wide temperature limits. However, by the assumption of the same relation of friction to the temperature for non-metallic substances n increases greatly with increasing temperature.

The rate of flow increases with increasing pressure more than proportionally both for metals and non-metals. This may be explained by presuming that n , the number of glide planes per unit of length, increases greatly with increasing pressure or that the friction in the glide planes decreases greatly.

The tendency to form glide planes determines then whether a crystalline conglomerate possesses plasticity or not. If the tendency to form glide planes is lacking the material is brittle and cannot be worked. However, small amounts of impurities and the temperature have an influence on the tendency for glide plane formation. Therefore, the last word is still not spoken concerning the workability of a material, which prepared in a certain way is found unsuitable for working at ordinary temperatures. Kick (*Sitzungsberichte des Vereins z. Förderung d. Gewerbfleißes* 1890, p. 11) has even stamped coins out of marble, since calcite does not lack glide planes and the stratification of the conglomerate does not prevent the deformation in a skillful manner. The greater the ability of a material to form glide planes the greater is its deformability. In many cases this ability decides its usability.

The plasticity of a crystallite conglomerate is accordingly determined (1) by the number of systems of glide planes (2) by the orientation (3) by the direction of displacement along the glide planes (4) by the number n of glide planes and (5) by the friction on the individual glide plane systems. Since the deformation elements are only partially known for single crystals in favorable cases, we are still far from being able to deduce from these partial determinations the behavior of a crystallite conglomerate on permanent deformation.

3. The Relation of the Malleability to the Chemical Nature of the Body.

The crystallite conglomerates of the metallic elements and their solid solutions are characterized by their plasticity.

The greater number of the metals have the same kind of lattice, which is a cubic lattice with atoms at the corners and centers of the

faces of the cube. However, metals which occur with other lattices, such as hexagonal zinc and tetragonal tin, show a quite high degree of plasticity. High plasticity and the corresponding ease of glide plane formation is accordingly not conditioned by the kind of space lattice.

In any event there are today only V, Cr, Mn and U to be named as brittle metals, since Ta, Nb, W and Mo are found to be plastic by the manufacture of metal filament lamps. It is, however, probable that pure V and Mn, which have the space lattice of ductile metals, are somewhat plastic and if Cr and U have either this lattice or that of tungsten this same probability holds for them. For solid solutions of Mn and Cu the occurrence of glide planes has been established up to high Mn contents.

A great difference is apparent if the metallic elements and their solid solutions are compared with the binary metallic compounds as regards their plasticity at ordinary temperature. Of about 100 binary

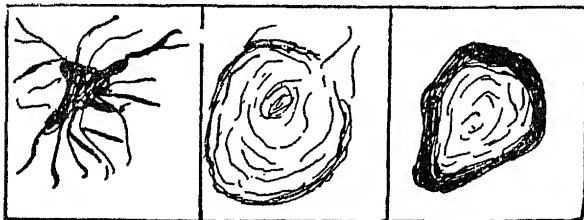


FIG. 38

metallic compounds not one shows traces of plasticity at ordinary temperatures; they are as a whole extraordinarily brittle. Since, however, these compounds are not infrequently formed from metallic solutions with rounded crystals, as for example the crystals, FeSi , NiSb , PdPb_2 , PdPb , Pd_2Pb , Ag_3Sn , CoAl , Ni_3Sn_2 , Co_2Sn , CoSi , CoSb , they must be plastic at the temperature of precipitation. The metallic elements and their solid solutions are accordingly characterized by the possession of plasticity at relatively low temperatures, while the binary metallic compounds lose their brittleness only at temperatures not far below their melting point. In this respect the binary metallic compounds resemble other compounds which are frequently plastic in the neighborhood of their melting point.

A comprehensive investigation concerning the behavior of metallic compounds on deformation (Dahl and Tammann, *Z. anorg. Chem.* 126, 104 (1923)) has shown that at ordinary temperatures compounds as a rule form glide planes as well as cracks; with CuMg_2 , Fe_2Sb_3 , FeSb_2 , Zn_3Sb_2 , ZnSb only cracks form. Compounds which show good cleavage, like Cu_3Sn and PbS , lose their cleavage at high temperatures and the tendency to form glide planes already present at ordinary temperatures is increased to plasticity. At sufficiently high temperatures

the compounds are plastic. On cooling to ordinary temperature the original brittleness returns.

The transition from brittleness to plasticity with increasing temperature is illustrated in Fig. 38 (110 diameters) for the compound Cu_2Cd_3 . At 150° numerous cracks radiate out from the point of impact. At 200° the point of impact is surrounded by a slight elevation through which goes a single crack. At 400° there are no cracks and the elevation is quite pronounced.

The occurrence of plasticity with increasing temperatures is given in Table 5; below a certain temperature t a piece of the material pressed between two parallel planes breaks to pieces while above this temperature the piece forms a rounded surface with no cracks.

TABLE 5

	Melting Point	t
Cu_3Sn	730°	$650^\circ \pm 30^\circ$
Sb-Sn (45% Sb)	420°	$350^\circ \pm 20^\circ$
NiBi	700°	$650^\circ \pm 20^\circ$
NiBi_2	480°	$450^\circ \pm 10^\circ$
NiAl_2	850°	$750^\circ \pm 30^\circ$
AlAg_2	725°	$450^\circ \pm 50^\circ$
AlAg_3	770°	$600^\circ \pm 20^\circ$
PbS	1100°	$700^\circ \pm 40^\circ$

With the following compounds plasticity does not occur so sharply, the surfaces of the test pieces cracking at the temperature of slight plasticity.

TABLE 6

	Melting Point	t
Cu_2Zn_3	830°	$700^\circ \pm 30^\circ$
Cu_2Cd_3	564°	$500^\circ \pm 20^\circ$
Cu_3Sb	670°	$600^\circ \pm 20^\circ$
Fe_2Sb_3	1010°	$800^\circ \pm 30^\circ$
FeSb_2	710°	$650^\circ \pm 20^\circ$
Zn_3Sb	560°	$450^\circ \pm 20^\circ$
ZnSb	520°	$400^\circ \pm 20^\circ$
CuAl_2	590°	$550^\circ \pm 20^\circ$
CoSn	950°	$800^\circ \pm 20^\circ$

Finally in the following bodies the transition from brittleness to plasticity takes place over a large interval.

TABLE 7

	Melting Point	t
Al_2Cu	900°	$800^\circ \pm 20^\circ$
CuMg_2	570°	$400^\circ \pm 20^\circ$
CoSb_2	900°	$800^\circ \pm 20^\circ$
$\text{Co}_3\text{Al}_{13}$	950°	$800^\circ \pm 30^\circ$

The difference between the temperature of melting and the beginning of plasticity amounts to 400° for PbS while the smallest difference, 30° , is found in NiBi₃.

In non-metallic bodies the tendency to form both glide planes and cleavage planes frequently occurs. J. Stark (*Jahrbuch der Radioaktivität* 12, 292 (1915)) has given the properties an atomic explanation which will be discussed in the following case of a NaCl crystal. In NaCl the positively charged Na atoms and the negatively charged Cl atoms have a cubic lattice; on the lattice lines parallel to the cube corners the two kinds of atoms alternate. If a knife is placed on a NaCl cube parallel to a cube corner and struck a sharp blow the

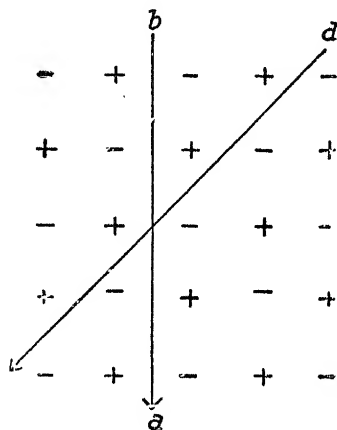


FIG. 39

two parts of the crystal are displaced a little. Hereby two similarly charged atoms are brought into the nearest proximity. At this moment on the entire plane ab (Fig. 39) only similarly charged atoms are in juxtaposition and as a result of the electrical repulsion the crystal parts. If on the other hand a force is applied parallel to a dodecahedral plane and its longer diagonal, i.e. parallel to cd (Fig. 39) and the plane of the drawing, gliding occurs and there is no separation along cd since alternate lines parallel to cd have only Na or Cl atoms; therefore the electrical action of the two planes on each other is not changed.

Finally the fact still remains unexplained that the octohedral planes are not glide planes. Since the alternate lattice planes parallel to the octahedral planes have only one kind of atom it is to be expected that the octahedral planes would be at least as easy to displace as those of the rhombic dodecahedron.

4. The Origin of Conchoidal Fracture.

A crack can be directed in a glass plate at will by heating a place on the plate by contact with a hot body. The crack always travels toward the heated spot where the pressure is the higher. If by striking a piece of glass longitudinal waves are set up and in this way fractures formed, these fractures are deflected from the positions of high pressure of the wave surface. Hence on the broken surface concentrically around the place struck subsidiary wave hills and valleys form, whose height and depth decrease from the place struck since the damping of the longitudinal waves is considerable. If the broken surface was originally a plane we may determine by counting the wave valleys in the fracture whether they correspond to a reinforcement or an attenuation of the longitudinal waves, since the first half wave corresponds to a reinforcement. However, the original fractured surface is as a rule so irregular that such a determination cannot be made. It can be seen from a fractured surface that by breaking a specimen not only longitudinal vibrations of a single wave length but frequently many wave systems with wave lengths varying from 1-100 mm. result. No matter whether the body is a homogenous glass, a single crystal or a conglomerate of crystallites its fractured surface will be conchoidal if only the crystallites lack cleavage and the ability to form glide planes is small. In fact we find under these conditions a typical conchoidal fracture in crystallite conglomerates, as in aluminothermically prepared manganese and many metallic compounds. Since the cleavage of crystals may be very different all transitions from conchoidal to granular fracture may be observed in crystallite conglomerates. Not infrequently rays occur on conchoidal fractures that run out radially from the place struck, i.e. vertically to the wave hills and valleys on the fracture. The cause of their formation is to be sought in a distortion of the longitudinal waves due to inhomogeneities or other causes.

5. Is the Space Lattice Changed by Permanent Deformation of a Crystal?

This question has been asked many times recently with reference to an X-ray diagram published by F. Rinne. (*Berichte der Königl. Sachs. Ges. d. Wiss. zu Leipzig* (1915), p. 303.) Rinne allowed a bundle of X-rays to fall on a photographic plate through plates of rock salt and Kainite. By permanent deformation the interference pattern changes. Rinne has shown, however, that by such permanent deformation single particles of the plates rotate about each other and that every rotation of a penetrated layer changes the interference pattern greatly. Therefore, the process of v. Laue is not suited to decide the question since it does not differentiate between a change by displacement of the particles of the plate with respect to each other and an actual change in the angle of the lattice and the distance

between the atoms. By the process of P. Debye and P. Scherrer (*Göttinger Nachrichten* (1916), p. 1-36), a bundle of X-rays is passed through a narrow paper case filled with crystal powder or through a wire that consists of fine crystals. Intensification of the rays takes place if the path between two planes of the space lattice whose distance is d , $2d \sin \theta$, is equal an even multiple of the wave length of the Roentgen rays λ . For a given value of λ and d , the angle of incidence for reinforcement through interference is determined by the equation $2d \sin \theta = n \lambda$. Reinforced reflected rays from one kind of lattice plane must all have the same angle of incidence and since for different kinds of planes the value of d is different, only rays of certain angle intervals will be reflected. The wire to be investi-

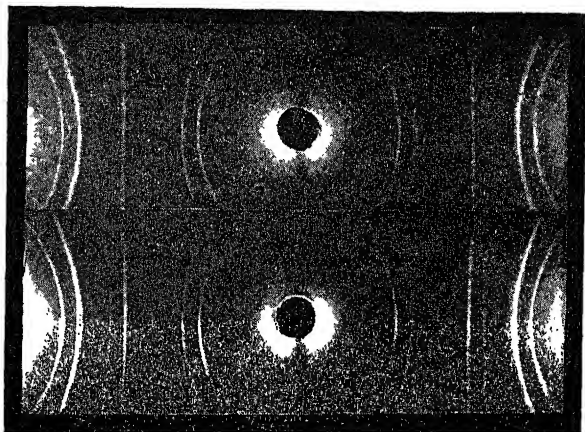


FIG. 40

gated is placed in the middle of a cylinder of roll film and a bundle of X-rays passed through it. The reinforced reflected light then goes out from the wire in cones and at the intersection of the cones with the plane of the film are black lines. Prof. Scherrer was good enough to examine hard and soft wires of a Cu-Au alloy with 0.25 mole Au and an Ag-Au alloy with about 0.25 mol. Au. Figs. 40 and 41 give the films at half the natural size. The lower half of both figures represents the soft wire. Both hard wires were prepared from buttons that were annealed 12 hours at 760° before working and then worked down without intermediate annealing; they were therefore of maximum hardness. The hard wires were then softened by long heating at 760° in an H_2 stream, the Cu-Au wire being annealed 2 hours and the Ag-Au wire 9 hours.

The bright lines of both illustrations correspond to the black lines of the original film. If the two original films are laid over one another and a black line brought to coincidence all the other inter-

ference lines fall together. With soft Ag-Au wire the white lines consist of many small points since by long annealing the crystallites have grown and their number is accordingly much smaller. If we consider that the Roentgen rays only penetrate the outer especially hardened layers of the wire it is seen that a maximum hardening does not affect the position of the black line and therefore not the size of d . Even if a change of the lattice parameter cannot be brought about by so great a deformation of Cu-Au and Ag-Au solid solutions, certain properties of the atoms themselves may change. In fact these solid

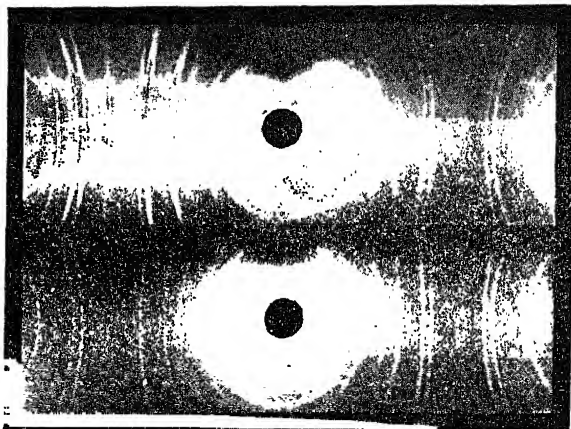


FIG. 41

solutions are made less noble by working and certain properties of the atom on which the chemical and galvanic properties depend are accordingly altered.

In the deformation of rock salt crystals along their translation planes a weak double refraction appears according to Reusch, while with calcite that forms twinning lamella by deformation a change in the optical properties is not found. Accordingly if with metals the lattice itself remains intact, changes which are of a secondary nature and which exert different influences on different properties may still go on in the atom.

6. The Elastic Limit and Flow.

The elastic limit of a crystal is determined by the direction of the acting force with respect to the direction of gliding. Its determination accordingly involves three angles and the magnitude of the force. The elastic limit of a crystal, the force at which gliding takes place in the crystal depends to a considerable degree on the orientation of the force toward the crystal.

Since in a conglomerate the crystallites are oriented irregularly, for a definite direction of the deforming force permanent displacement will only occur in the favorably oriented crystals, while those with unfavorable orientation are only deformed after a very considerable increase of the force. If finally the conglomerate has still a sufficient amount of mobility, i.e. a sufficient number of displacements can take place, flowing occurs. There is to be expected accordingly in plastic crystalline conglomerates a great difference between the force at which the first permanent deformation is shown and that at which flow occurs.

If the pressure on a metal cube is increased cautiously, and one side parallel to the direction of pressure polished, it is seen that in the middle part of the surface in which the pressure field is the most homogeneous, the crystallites in which the first glide lines appear lie practically vertical to the direction of pressure. With further increase of pressure new glide lines become visible in other crystallites, whose angle with the direction of pressure decreases as the pressure is increased. Then there appears in the crystallites where glide lines are already present still other glide lines at an angle to those present. Corresponding to the different orientations with respect to the direction of pressure, displacements occur in the crystallites one by one, and of course first in the crystallites whose orientation is the most favorable. These crystallites are relieved from the load by the displacements, accordingly fewer crystallites have to carry the load, so the pressure is increased till displacement takes place in a second group of crystallites. In this way the elastic limit increases, since the crystallites in which no gliding has taken place carry the principal part of the load, which their orientation with respect to the surrounding crystallites enables them to do. After gliding in all the crystallites of the conglomerate a new displacement takes place only after exceeding the highest pressure value which the conglomerate requires. The greater the number of glide planes in unit volume along which the displacement has taken place the higher is the elastic limit of the worked piece and the greater the degree of working.

Further the size of the grains in the conglomerate has an effect on the elastic limit. If two conglomerates of the same metals with different crystal sizes are compared, the conglomerate with smaller grains has a higher elastic limit than the one with large grains. Also fine grained eutectics have a higher elastic limit than the coarse grained crystallite conglomerates of their components.

These facts can be explained by the fact that with the same loading the field of force in the crystallite conglomerate becomes more homogeneous with decreasing crystal size.

Also the increase of the elastic limit after the previous exceeding of the same is a result of the decrease in size of the grains by glide surface formation and the consequent homogenizing of the inner field of force. Microscopic investigation of the displacements which occur

inside of the crystallite conglomerate by the action of an external homogeneous field of force gives us a knowledge of the inner field of force. The greatest number of lines of force originally passed through the crystallites in which the first displacements occurred. As a result of the displacement these lines are divided among the neighboring crystals.

7. The Microscopic Method for Determining the Elastic Limit.

The occurrence of displacements or glide surfaces in crystallites by working of their conglomerates may be considered as characteristic of permanent deformation, accordingly also as characteristic of the exceeding of the elastic limit. (O. Faust and G. Tammann, *Z. physik. Chem.* 75, 108 (1910).)

The method of determining the elastic limit which is based on the microscopic observation of a polished surface of a piece of metal slowly deformed by pressure or tension shows by what process the elastic limit is exceeded, whether glide plane formation or crystallite displacement occurs and whether accordingly the strength of the crystallites is greater than their adhesion or whether the reverse is true.

In the following tables the observations are collected (O. Faust and G. Tammann, *Z. physik. Chem.* 75, 111 (1910); G. Tammann, *Z. physik. Chem.* 80, 687 (1911)) concerning the kind and method of permanent deformation which takes place in cubes of several metals by the action of compression or tension parallel to a polished side of the cube. To bring the metals in their natural condition with the least possible elastic limit, the higher melting metals were heated for $\frac{1}{2}$ hour at 100-200° below their melting point. With gold and copper glide lines occur first while with Ag the occurrence of glide lines is simultaneous with the displacement of the crystallites. In the case of the three most ductile metals then the conglomerate strength is accordingly greater than the strength of the crystals. This is especially true for Au and Cu, while with Ag the two strengths are almost equal.

With other metals the strength of the conglomerate is not greatly below that of the crystallites; with Fe, Ni, Zn and Mg displacements of the individual crystallites occur first and glide lines form only with considerably increased work. With Al, Sn and Cd conglomerates of crystallites stand out on the polished surface.

If a metal is worked beyond its elastic limit by slow increase of the compression or tension and the observation plane is again polished, we see by further working the marks of permanent deformation, crystallite displacement or glide lines occur again at the highest pressure of the first experiment. In this way the pressure of permanent deformation can be increased up to a limiting value at which the cube begins to flow. This process is somewhat time consuming but it gives the flow pressure within narrow limits. The result may be reached

TABLE 8

Metal	Previous Treatment	U = Elastic Limit	Remarks	O = Flow Pressure	Remarks	$\frac{O}{U}$
Gold	Heated to 1000°	46 kg./sq. cm.	$\frac{1}{2}\%$ Error 4 Exp.			
Silver	Cast, heated to 800°	86 "	4% Error 2 Exp.			
Copper	Melted, cooled slowly	203 "	1% Error 16 Exp.	2780 kg./sq. cm.	6% Error 4 Exp.	13.7
Copper	Melted, cooled fast	350 "				
Aluminum	Melted in stream of H ₂ , cooled slowly	283 "	5% Error 11 Exp.	600 "	6% Error 6 Exp.	2.33
Lead	Melted, cooled slowly	25 "	8% Error 4 Exp.	102 "	8% Error 4 Exp.	4.08
Iron	Well annealed	2370 "	1% Error 6 Exp.	5840-6000	4 Exp.	2.46
Cadmium	Melted, cooled slowly	27.7 "	$\frac{1}{2}\%$ Error 4 Exp.	109 "	8% Error 4 Exp.	3.61
Magnesium	Heated 1 hr. at 1600° in H ₂ stream	118 "	10% Error 6 Exp.	580 "	8% Error 4 Exp.	4.92
Nickel	Heated 1 hr. at 1350°	788 "	6% Error 4 Exp.	5570 "	10% Error 4 Exp.	7.78
Tin	Melted, slowly cooled	34 "	1% Error 4 Exp.	54.8 "	3% Error 3 Exp.	1.64
Zinc	Melted, slowly cooled	124.5 "	$\frac{1}{2}\%$ Error 4 Exp.	770 "	5% Error 4 Exp.	6.85
Zinc	Melted, cooled quickly	220 "				

more quickly, if the pressure on the cube is raised at once above the flow pressure, and the pressure observed which by constant lowering of the pressure appears as the limit of flow pressure. If this pressure has been determined it can be shown by microscopic observation that by a small excess over this pressure the characteristics of permanent deformation appear on a freshly polished face. For the reduction of the observed pressure to a unit of surface the cross section of the cube at the finish must be measured.

By the action of tension the same values of the elastic limit are found as by compression.

TABLE 9

	Elastic Limit	
	Action of Tension	Action of Compression
Nickel	791.9 kg./sq. cm.	788 kg./sq. cm.
Copper	203.8 "	203 "
Zinc	122.75 "	124.5 "
Cadmium	27.3 "	27.7 "

Also the microscopic appearance of the action of tension is very similar to that of the action of compression. (See table on page 81.)

8. Hardness.

While the elastic properties of a crystallite conglomerate as shown by the Brinell hardness and rebound hardness, its yield point, and its tensile strength, increase with cold working, the hardness of the individual crystals, as shown by the scratch hardness, is not changed. For three kinds of brass with 28, 37 and 40 per cent. Zn, F. Körber and Wieland have found the following values. (*Mitteilungen des Inst. f. Eisenforschung, Düsseldorf, III, p. 57 (1921).*)

	Degree of Rolling, in %	Scleroscope Hardness	Brinell Hardness, Kg./mm. ²	Width of the Scratch in 00/mm.
28% Zn	0	46	52	11.0
	15	36	95	11.0
	30	42	120	10.8
	50	52	130	10.6
	75	62	150	10.8
37% Zn	0	17	51	11.0
	15	28	86	11.0
	30	36	104	10.8
	50	43	124	11.0
	75	55	137	11.0
40% Zn	0	20	61	11.2
	15	35	83	11.2
	30	47	124	11.0
	50	54	141	11.0

Also according to O. Faust and Tammann (*Z. physik. Chem.* 75, 123 (1911)) the scratch hardness of copper does not change on cold work.

Accordingly the elastic properties of small particles are not changed while the form of the entire conglomerate and the orientation of the crystallites is very greatly changed.

The hardness of a brittle isotropic body can be evaluated in absolute units according to H. Herz, in the following way. If a spherical surface of a substance is pressed against a plane surface of the same substance a circular indentation is formed at the contact. The load P is increased till a crack forms at the center of the indentation. The pressure P_1 at the center of the indentation at the moment of fracture is the hardness of the substance. If q is the surface area of the indentation and D its diameter P_1 is given by

$$P_1 = \frac{3}{2} \frac{P}{q} = \frac{3}{2\pi} \frac{P}{\left(\frac{D}{2}\right)^2} = \frac{6}{\pi} \frac{P}{D^2}$$

Accordingly the pressure is distributed from the center of the impression, where it is greatest, to the periphery, where it is nil, proportionally to $\sqrt{1 - \frac{x}{r}}$ where r is the radius of the impression and x the distance of the point from the center.

By this method F. Auerbach (*Wied. Ann.* 43, 60 (1891), 58, 380 (1896)) has determined the hardness of the minerals of the Mohs' scale.

Auerbach found that P_1 is inversely proportional to the cube root of the radius of ball pressed against the plate. The values of P_1 given in the following table are with a ball of radius 1. The minerals in the Mohs scale are prefaced with the hardness numbers.

TABLE 10

Mineral	Hardness kg./sq. cm.	Mineral	Hardness kg./sq. cm.
1 Talc	500	5 Apatite	23,700
Gypsum	1,400	6 Adularite	25,300
2 Rock salt	2,000	Borosilicate glass	27,400
3 Calcite	9,200	7 Quartz	30,800
4 Fluorite	11,000	8 Topaz	52,500
Heavy silica flint.....	17,000	9 Corundum	115,000
Light silica flint.....	21,000.	10 Diamond	?

The conditions for measuring absolute hardness values are best fulfilled by isotropic and brittle glasses. With plastic materials like rock-salt, fluorspar, calcite and especially metals, the pressure on the surface changes according to a law other than that for brittle glasses. The pressure is more uniformly distributed by the plastic substances than by brittle since in plastic substances the permanent displacements are greater the nearer the displaced part is to the center of the depression.

Further the plastic materials become hardened by their deformation

and therefore appear harder. Auerbach has shown, however, that with increasing load P for plastic substances $\frac{P}{q}$ approaches a constant limiting value and has based the calculation of P_1 on this value.

In any case the hardness in kg./sq. cm. does not have the same meaning for plastic and brittle substances. The hardness of the plastic materials appears too large relative to the brittle. This method of measuring hardness is however more free from arbitrary factors than scratch tests.

The following table gives the determinations for several metals according to Auerbach (*Ann. Phys.* 3, 108 (1900)).

Metal	Hardness in kg./sq. cm.	Comparable Mineral
Tool steel	36,100	quartz
Phosphor copper	14,300	apatite
15 pts. Cu and 2 pts. Zr and 1.5 pts. Sn....	12,700	
66% Cu and 34% Zn.....	10,700	fluorspar
Au	9,700	calcite
Cu with 0.4% P.....	9,500	
Ag	9,100	boric acid
Al with 6% Cu.....	5,200	
Pb	1,000	gypsum

The hardness determined in this way is considerably greater than the flow pressure (see p. 84) since during deformation in the hardness test particularly the central part of the impression cannot evade the pressure as in the determination of flow pressure. Therefore in the hardness determination a maximum hardening is reached.

Closely related to the method of H. Herz is the Brinell method which is used in practice. Brinell presses a steel ball of 10 mm. diameter against a plane of the material under test, using pressures of 3000, 1000 and 5000 Kg., according to the hardness of the material, and measures the indentation. The pressure divided by the surface area of the indentation gives the Brinell hardness.

The falling ball test, by which the rebound of a hammer allowed to fall on the piece to be tested is measured, is also used considerably. It is to be remarked that the ratio of rebound to the height of fall is 0.4 for rubber and 0.38 for soft iron so that according to this test rubber is harder than soft iron.

9. The Relation of the Deformation to the Acting Force.

For studying this relationship various kinds of apparatus have been constructed which automatically record the deformation of the test piece in a definite direction with relation to the increasing force. We are here interested principally in the way in which the inner structure is revealed by the curves which represent the relation of the deformation to the force.

Figures 42, 43, 44 and 45 give the relation of the elongation to the load for the unit of original cross section in Kg. per square cm. on specimens of steel, copper and brass according to C. Bach (C. Bach, *Elastizität und Festigkeit*. Springer (1898)). The elongation

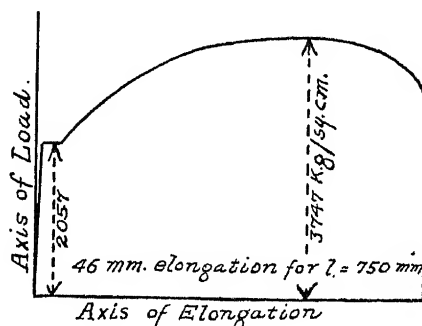


FIG. 42

Round rod of ingot iron investigated after exceeding the elastic limit only once

with increasing load is at first very small and increases proportionally to the load. In this region the deformation is reversible. Then follows the region of small permanent elongation in which the elongation increases somewhat more rapidly. After this there follows with

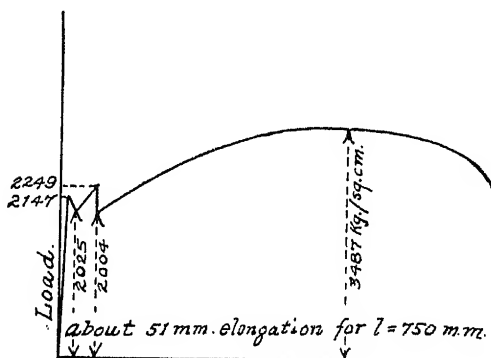


FIG. 43

Round rod of ingot iron investigated after exceeding the elastic limit only once

steel a region of irregular elongations which is lacking in copper, brass and bronze. If we more rationally reduce the constantly acting tension to the momentary cross section of the most narrow place in the test piece, the tension-elongation curves for steel, copper and brass are more similar. The practically horizontal places in the curves

are those at which the piece changes so that with increasing elongation the tension per unit of cross section increases greatly. In the region of proportionality no changes in the inner structure are observed, neither displacements of the crystals with respect to each other nor the formation of glide planes in the crystallites. The first

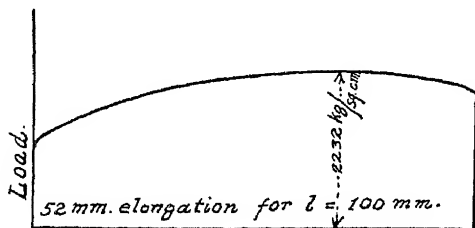


FIG. 44

Round rod of copper investigated after exceeding the elastic limit a number of times

permanent elongation is caused in copper and its alloys by displacements in the crystallites along glide planes, while with steel the noticeable irregularities of the elongation which occur right after the elastic limit is exceeded, are obviously caused by displacements of the crystals with respect to each other. These displacements are

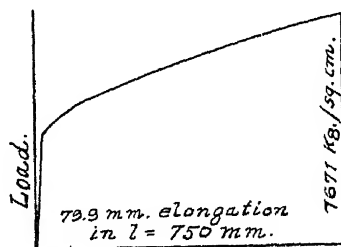


FIG. 45

Round brass rod investigated after exceeding the elastic limit a number of times

more irregular than the displacements along glide planes since we have to deal with larger structures than with the displacement along glide planes.

The diagrams Figs. 42, 43, 44 and 45 refer as mentioned not to a tension that acts per unit of cross section at the narrowest place on the piece but to constant tension with variable cross section.

If the cross section of the piece is measured during the tension or compression tests and the acting load referred to a unit cross section when this is plotted against the percentage reduction of the original

cross section with a tensile test or to the percentage decrease of the original length in a compressive test the curves shown in Fig. 46 are obtained. These measurements of Moellendorf and Czochralski (*Zeit. d. V. d. Ing.* (1913), p. 931) were carried out on copper. The lower curve refers to annealed copper. Point E is the elastic limit, at point 1 the stretching is apparent, point 2 is the highest load of the load-elongation diagram (Fig. 44) and point 3 is the breaking load. The other curves refer to cold worked copper; with increasing working, point 1, at which stretching begins, is displaced to higher tensions. Between points 2 and 3 the curves are practically straight and their

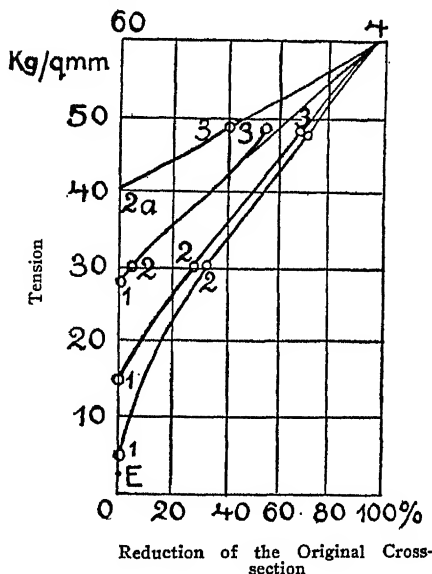


FIG. 46

linear prolongations meet in a point at which the pressure is twice that of the point 2.

The hardening by permanent deformation is also explained by the following experiment.

Bridgman (*Phys. Rev.* 43, 1 (1912)) cemented a tube in the central bore of a cylinder of steel, filled the bore with mercury and subjected the cylinder to hydrostatic pressure from without. In Fig. 47 the percentage reduction in volume of the bore in relation to the hydrostatic pressure is shown.

The elastic deformation to 2000 Kg. is followed by a permanent one. The elastic limit of the soft iron cylinder is 2000 Kg. If the pressure is increased above this, the elastic limit is raised so that on compressing the material again up to the highest pressure reached

in the previous experiment it is again elastically deformed and only by exceeding this does permanent deformation occur. With increasing pressure the increment of pressure for a definite amount of permanent deformation decreases. At 6000 Kg. the volume of the bore changes from 0.24-0.26% with practically no pressure change, which corresponds to the definition of the flow limit: (Table 8.)

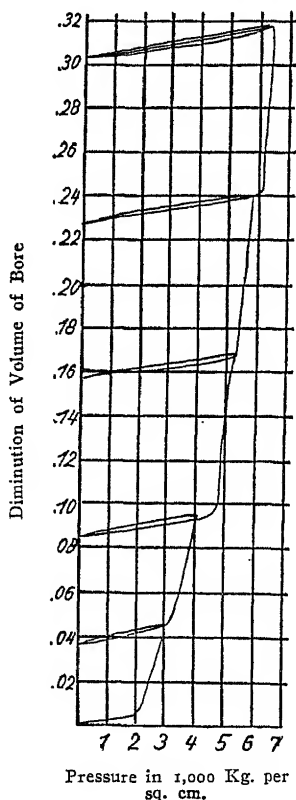


FIG. 47

By cold working the material can accordingly be extraordinarily hardened. Thereby, however, a great breaking down of the material by internal displacements is found, whereby the material becomes brittle. It is accordingly to be expected that impact, notch and bending tests on hardened material will give less favorable results than on unhardened material. The materials which give a maximum hardness with the least possible increase of their brittleness are still to be found.

In practice the hardening of metals by cold work is used relatively seldom. Cannon tubes of Uchatius Bronze were previously hardened from the inside out by this method.

The hardening of materials on deformation takes place however only for a definite kind of treatment. If a treatment by tension is followed by one of compression the elastic limit for a second treatment is not increased but lowered. Fig. 48 gives an ideal diagram

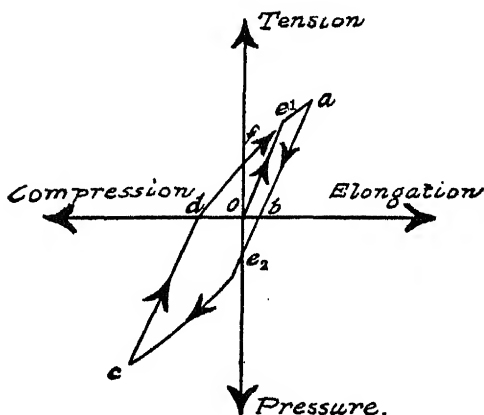


FIG. 48

on the basis of the observations of Bauschinger. (*Mitteilungen a. d. Mech.-techn. Labor der polytechnische Schule zu München*, 13, 31 (1886).)

The test piece changes its length with increasing tension along the line $oe_1\alpha$. The elastic limit is e_1 . When the tension is released the piece is permanently elongated to the length ob . Now by deformation through compression permanent shortening of the piece takes place on exceeding the point e_2 . After the point c is reached the pressure is lowered. At zero pressure a permanent shortening od exists. If the piece is again stretched its length increases more rapidly at lower tensions than on the first treatment, namely along df . The elastic limit by this treatment becomes vanishingly small.

10. Hardening above the Flow Limit.

It was mentioned that the maximum load on pulling a test piece in Fig. 44 corresponds to point 2 in Fig. 46. Fig. 49 gives the results of F. Körber (*Stahl u. Eisen*, 42, 365 (1922)) for copper and various kinds of steel, the tension per unit of actual cross section being plotted against the per cent. change in cross section. These changes of cross section refer to the point of greatest reduction. We see that in the field of strong plastic deformation the tension is directly proportional

to the cross section decrease. In Fig. 49, point 2 corresponding to the maximum load in Figs. 42-45 is not especially evident. Up to this point the increase of strength is explained as due to the homogenizing of the inner field of force. This is due to the displacements of crystallites along their planes. For the hardening above point 2 F. Körber gives the following diagrammatic explanation. We consider that during the flow of the material, starting at point 2, there is an orientation of the crystal elements with respect to the direction of deformation. This takes place in the way that those planes along which gliding takes place most easily are rotated to positions less favorable. Accordingly for further deformation the outer force must be increased till its component again reaches the displacement strength.

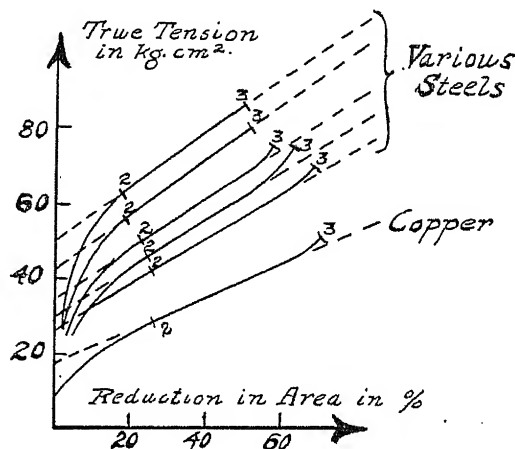


FIG. 49

The glide planes will accordingly after drastic deformation be parallel to one another, but a definite angle to the deformation axis will be present.

F. Körber advances a clear argument for this conception. A crystal conglomerate in which the crystallographic directions have a definite angle to a given axis must behave in a Debye-Scherrer diagram as a single crystal rotated about this axis. All the lattice planes that are inclined to the axis of the incident rays at less than the characteristic glancing angle will appear on the film only as spots in place of the lines obtained by irregular distribution. If the crystallographic elements are not all equally oriented the same spots will not occur but the intensity of the interference lines will be considerably increased in places. Polanyi (*Z. f. Phys.* 5, 61 (1921), 7, 181 (1921)) first observed and recognized this fibrous structure of hard metal wires. Körber assumed as Wever has found for Fe and Cu that in general

the most thickly packed planes present the greatest ease for gliding. These become oriented vertical to the fibre axis.

Especially with α iron the elements of the original crystallites divided by glide planes are rotated so that the rhombic dodecahedral face (011) is parallel to the direction of force. If we conceive of a cubical element at a definite orientation to the direction of force it will finally rotate into the position shown in Fig. 50. Here the face diagonals of the cubical element coincide with the direction of

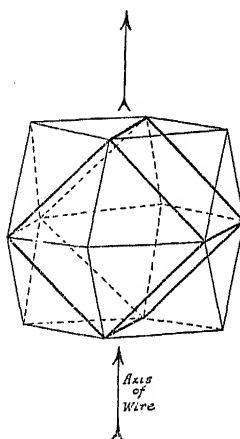


FIG. 50

force which accordingly falls in the rhombic dodecahedral plane. In this position the cubical elements are grouped around the direction of force. The gliding will not now take place along planes parallel or vertical to the deformation axis but on those which are inclined 30° to the direction of force. If a hard drawn wire is sectioned vertical to its longitudinal axis the lamellae are only cut along the rhombic dodecahedron. By etching the section it will reflect the light uniformly since the etch figures will all be similarly oriented, while on a section of annealed wire the etch figures vary from crystallite to crystallite and therefore the light is reflected in various ways.

11. Strains in Cold-Worked Metallic Substances.

By rolling of rods or plates, by wire drawing, by hammering and pressing, the various layers of the specimen are displaced with respect to each other. In this way compression and tension strains result in various layers. E. Heyn and O. Bauer (E. Heyn and O. Bauer, *Int. Z. Metallographie* 1, 16 (1911), Martens-Heyn, *Materialienkunde* 1A 280 (1912), E. Heyn, *Stahl u. Eisen* (1917) Nos.

19, 20, 21 (1917), have given the following method for measuring them. If the top layer of a metal cylinder I is turned off and the remaining piece II does not change its length there are no strains between the outer layer and the center. If the remaining center shortens, a tension was exerted upon it by the turned off layer; if the center elongates, we have dealt with the action of compression. If we consider the relative change of length by turning off for a unit length a piece $\frac{l-l_1}{l}$ we find if

$l > l_1$ the tension σ'' between outside and center is $\sigma'' = E \frac{l-l_1}{l}$,

since E the modulus of elasticity is the quotient of the tension by the relative dilatation. If we designate f' and f'' as the cross section of the outer layer and center respectively and σ' and σ'' as their tensions, for the original state the equilibrium condition $f' \sigma' + f'' \sigma'' = 0$ holds. If we substitute here the value of σ'' we get for the outer

layer the strain $\sigma = E \frac{f''}{f'} \frac{l_1-l}{l}$.

In a nickel steel rod with 25.1% Ni and 0.4% Cu the distance between two marks was measured after each layer of 0.5 mm. thickness was turned off between them. From the change in length of the piece the tension σ'' of the center was calculated and plotted in its relation

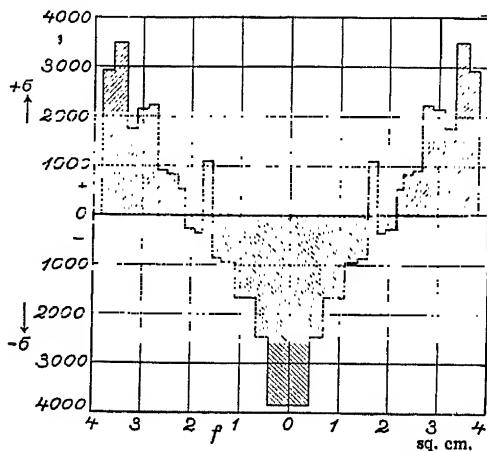


FIG. 51

to the half cross section f'' of the center. Fig. 51 gives the strains of the hard piece, and Fig. 52 that of the annealed (one hour at 850°). The tension strains are plotted above the zero line and compressive strains beneath it. The condition of the equilibrium requires the enclosed areas above and below the zero line to be equal.

In a cold worked metal rod there are accordingly tension strains

in the outer layers and compressive strains in the inner layers. These are reduced by annealing to a very small remainder. Also cold worked brass shows strains of about half those of nickel steel. If a cold worked brass rod of 20% reduction in area is immersed in mercury nitrate solution the piece breaks after 10 minutes with a sharp noise

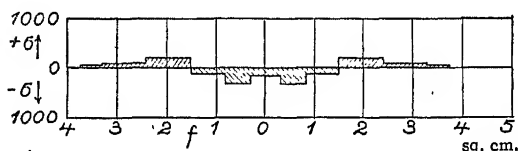


FIG. 52

and numerous longitudinal cracks. The cracks open wide apart on the surface indicating that the surface is in tension and the inner layers in compression.

The action of too great an amount of drawing on a steel wire is shown in Fig. 53 from Martens. (A. Martens, *Mitt. aus d. Kgl.*



FIG. 53

Techn. Versuchsanstalt, No. 10, p. 57 (1892).) The inner layers have been subjected to greater displacement than the outer and as a result inner cracks of the form of rotation paraboloids have formed.

According to Heyn the blue brittleness of steel is due to the working of steel at a blue heat between 150° and 300° which develops great strains.

12. The Recrystallization of Cold Worked Metals and Its Causes.

The original properties of a cold worked metal are either partially or completely restored by heating depending on the temperature and time of heating. It is, therefore, possible within certain limits to change at will the properties, especially the elastic properties, of cold worked metals. Changes in the microstructure of the metal are bound up with these changes. We find that upon heating to a high temperature the grain of a cold worked metal grows greatly and approaches the grain of the material obtained from a melt. This phenomenon has been explained in the following way: The vapor pressure of small drops is known to be greater than that of a larger plane. If this theoretical knowledge is carried over to large and small crystals we have a basis for the formation of large from small crystals. The increase of size of the grains, however, takes place with considerable

velocity at temperatures where the vapor pressure of the metal is still inappreciable, so that the grain growth as a result of a distillation process cannot be considered. In addition, the process of recrystallization goes on with the formation of especially small crystals between many 100 times greater lamellae. Accordingly the smaller crystals may form from the larger. We will return to the more pertinent explanations of recrystallization after acquiring a knowledge of the principal facts.

(a) Facts concerning the recrystallization of cold worked metals. Recrystallization begins by the formation of extraordinarily small new crystals in the fragmented mass of the crystallites of the cold worked piece; these crystals grow very slowly at the temperature at which recrystallization begins; at higher temperatures they

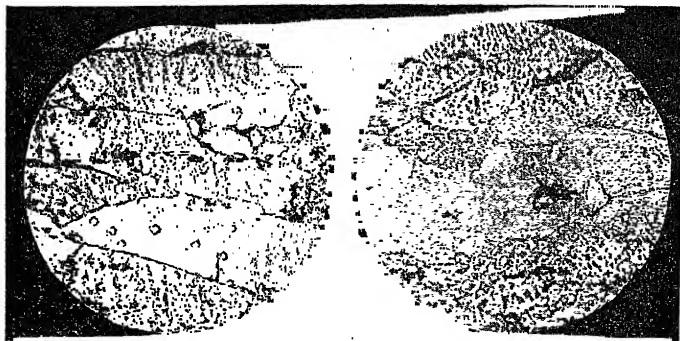


FIG. 54

FIG. 55

grow faster and faster. At the beginning of crystallization then we are dealing not with the recombination of the crystalline fragments by contractile forces, and not with the growing of the larger fragments at the expense of the smaller but with the formation of new crystals which are at first very small. If the temperature is increased by steps, each temperature change starts a crystal growth which, however, does not continue for long and sets in again with every rise of temperature.

E. Heyn (*Z. d. Vereins deutscher Ingenieure* 44, 433 (1900)) found that at the beginning of recrystallization, a smaller mean grain is present than before the cold working and that at high temperatures this grows rapidly. He determined the mean grain size in rolled steel, and afterward heated the piece to various temperatures and found

	In the Cross Section	In the Longitudinal Section
Original grain size.....	1,160 μ "	—
After rolling	353 "	650 μ "
After heating to 417°.....	—	600 "
" " " 616°.....	373 "	297 "
" " " 960°.....	—	1,100 "

The beginning of recrystallization in steel that according to Goerens proceeds rapidly between 520 and 580°, has been recognized by Chappel (*Ferrum* 13, 6 (1915)) as first starting between 350 and 500°. Between 500 and 570° small single grains with definite boundaries form in the lamellae of the cold rolled iron. These grow relatively rapidly and form as small polyhedra of about the size of the lamellae resulting from rolling. (See Figs. 54 and 55.)

The recrystallization of copper is shown in Figs. 56 and 57. In Fig. 56 we recognize the fibrous structure of a hard unannealed copper wire that consists of many thin lamellae that lie parallel to the direction of drawing. By heating the wire to 500° for 30 minutes

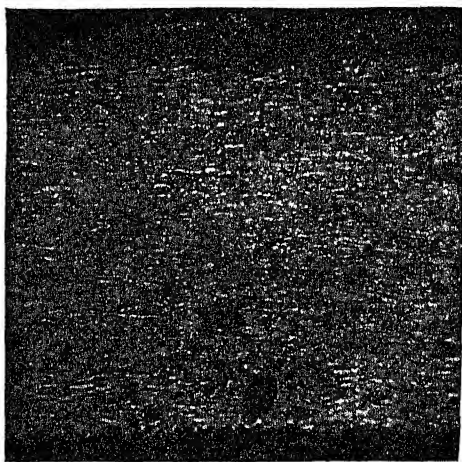


FIG. 56

Drawn copper wire. Etched with HNO_3 . $\times 120$. \rightarrow Direction of drawing

the fibrous structure completely disappears and numerous unoriented large and small crystallites are recognized (Fig. 57).

Figs. 59, 60 and 61 (O. Faust, *Z. anorg. Chem.* 78 (1912)) show the progressive changes which take place in the same piece of cast copper after great deformation, by successive heatings at always higher temperatures. To make the changes evident, we must after every treatment, whether by pressure or heating, polish the specimen and etch with ammoniacal copper chloride since the etched surface remains unchanged by heating in a stream of hydrogen or nitrogen even if important changes in the grain size take place within the conglomerate of crystallites.

The large crystallites of cast copper (Fig. 58) are divided into numerous small crystallites by drastic deformation of the specimen (Fig. 59). By heating to 650 and 700° the grain grows. With

further increase of temperature to 900° (Fig. 61) and 1050° (Fig. 61) the crystal growth still continues. The first start of recrystallization, the formation of new small crystallites, cannot be found from this series of observations, since this new crystal formation takes place in copper at 200° . The individual copper crystallites are attacked very differently by the etching agent since the solution rate depends greatly on the crystallographic orientation of the plane on which the etching agent acts. This fact brings out frequent formation of twins.

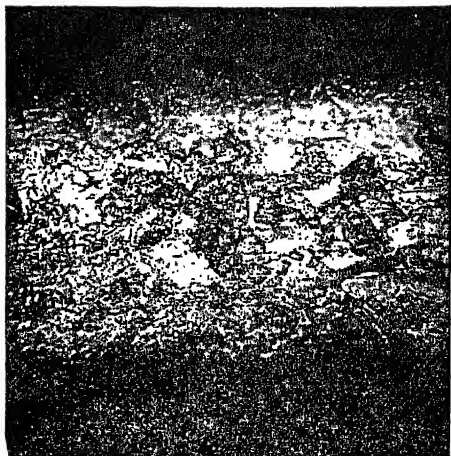


FIG. 57

Drawn copper wire after heating to 500° .
Etched with HNO_3 . $\times 120$

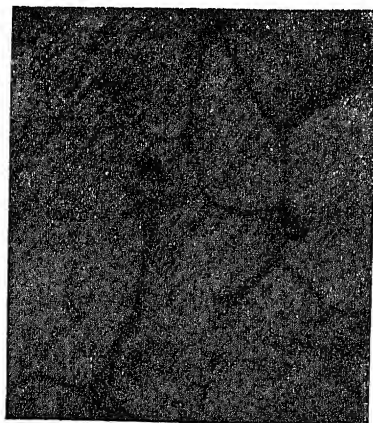


FIG. 58

Copper slowly cooled after melting.
 $\times 72$

The size of the grain developed after recrystallization depends not only on the temperature but also on the amount of deformation in the cold state. With iron the grain size at first increases with the deformation and then decreases greatly with increasing deformation. Chappel has drawn very important conclusions concerning recrystallization from broken iron specimens (Fig. 62). On the broken end where the deformation of the broken test piece was of course the greatest, there develops by heating to about 800° a smaller grain than in the less deformed places. Schwarz (*Intern. Zeit. Metall.* 7, 124 (1915)) broke a copper crystal and found that a great number of smaller crystals are formed around the break upon heating.

The grain immediately under the impression of a hard steel ball on a piece of soft iron, develops less on heating than that further down in the piece. (Fig. 63.)

In the LeChatelier Institute many experiments have been made on

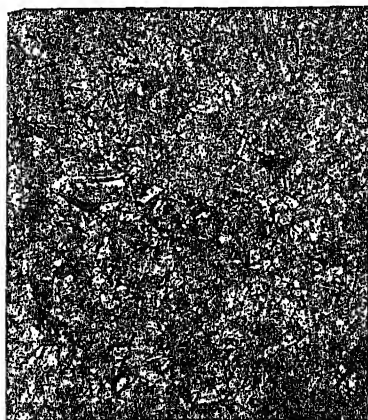


FIG. 59

Cast copper after considerable deformation. $\times 72$



FIG. 60

Copper, the same as in Fig. 59, heated to 900° for 10 seconds, showing recrystallization. $\times 72$



FIG. 61

Copper, the same as in Fig. 59, heated at 1050° for 20 minutes, showing further crystal growth. Further heating at 1050° produces no further growth of crystals. $\times 72$

the special phenomena of recrystallization by the process devised by him (Portevin, *Rev. de Met.* 10, 680 (1913); Robin, *ibid.*, p. 773).

Cold rolled plates of 1-0.1 mm. thick were heated in a stream of

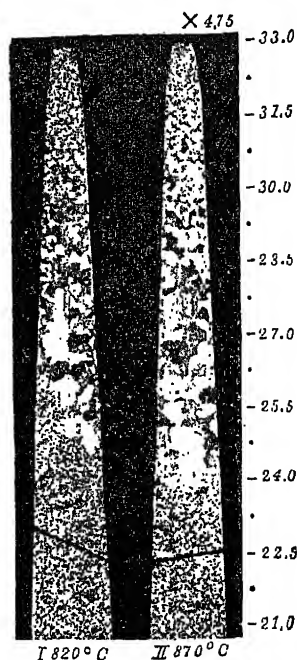


FIG. 62

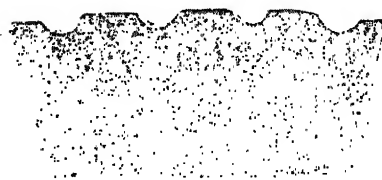


FIG. 63

hydrogen so that they were subjected to a temperature gradient. The temperature gradient in the plates reached from the melting point of the metal at one end to about 50° at the other. The influence of temperature on the grain size of the plates is made easily visible by appropriate etching of the polished surface, and from a series of

similar plates subjected to the temperature gradient for various times the influence of time and temperature on the grain size can be surveyed.

We may get an idea of the rate of recrystallization in the following way: if a hard plate is folded so that the fold is coincident with the direction of rolling and bent open again, a grain like that shown in Fig. 64 is produced by a temperature gradient; on the polished fold *ab* small crystallites form whose size noticeably decreases toward *b* with decreasing temperature. On both sides of the fold very large crystals form which extend the further from the fold the higher the temperature. Their boundary against the very fine grain of the steel not noticeably recrystallized is quite sharp. If the distance from the fold *ab* of the boundary between the fine grain and the large crystallites from *ab* is measured and this distance plotted in relation to the temperature, an idea is obtained of the rate of crystallization. We see that the kind of deformation has a great influence on the grain size and the velocity of its propagation. Along the fold

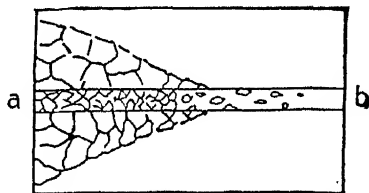


FIG. 64

in which the deformation was in two directions, the size of the grain is much smaller at the same temperature than that of the part only rolled. However, recrystallization will go on at the fold at a much lower temperature than on the surface and finally the fold is the place at which recrystallization starts. With tin recrystallization begins after $\frac{1}{2}$ hour at 45° ; up to 150° the new grains remain relatively small, then they rapidly grow large. The grain size and the velocity of their development depends on the thickness of the plates reaching a maximum at a thickness between 4 and 6 mm. The size of the crystallites increases rapidly below 120° for a duration of heating less than 20 minutes, with longer heating there is little change.

Lead behaves very similarly to tin.

Recrystallization takes place with zinc at 75° by the formation of relatively large crystallites. As the temperature increases the crystal size decreases up to 250° , above this the crystal size increases at first gradually but at 350° the crystal size increase with temperature has become rapid.

In rolled copper at 200° a large number of very small crystallites form which increase in size regularly with increasing temperature. The grain size increases with the thickness of the plate. Concerning the recrystallization of iron, we have the works of Tschernow,

Osmond, Stead, Heyn and others. The recrystallization begins to be important between 500 and 600°, the grain grows rapidly up to 620° then slowly a maximum is reached at 750° (transition point of $\alpha \rightarrow \beta$ iron 769°) then slowly decreases to 900°. At 900° (transition point of $\beta \rightarrow \gamma$ Fe 906°) the grain decreases according to all authors very rapidly and then with increasing temperature increases again.

Foreign metals lessen the size of the tin grains developed at 190°; the smallest addition producing considerable effect and further additions only a relatively small effect.

Heyn (Martens-Heyn, *Materialenkunde für den Maschinenbau*, II A.,

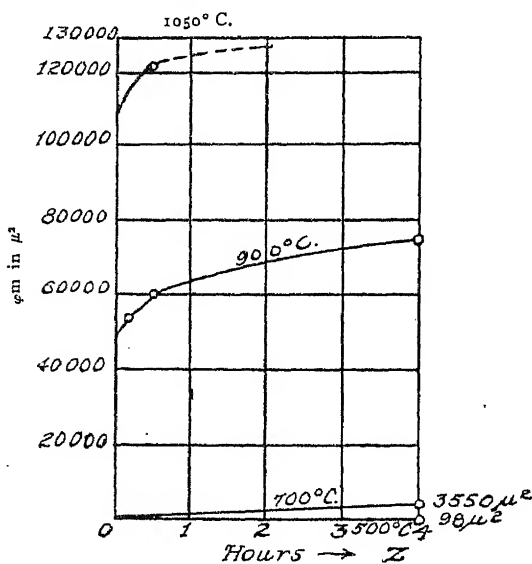


FIG. 65

p. 213 (1912)) has made comprehensive observations concerning the velocity of recrystallization of copper. In Fig. 65 q_m designates the size of the grain measured in μ^2 ($1 \mu = 0.001$ mm.) that has formed in a given time at three different temperatures. We see that the grain size does not increase at 500°, and very slowly at 700°, that at 900-1000° it begins increasing very rapidly and then grows slowly. The inverse relation holds for the number of grains in unit volume.

The strength of a conglomerate depends on the crystal size, decreasing greatly with too great grain size. Iron heated for a long time above 1000° is called "burnt" since it has had its strength greatly decreased by great increase of the grain size. The grain size can according to E. Heyn, be used as a maximum thermometer. If, for example, a boiler plate is bumped out, and the grain of the fracture

has grown considerably it is certain that at this place it has been heated above 650° .

The influence of the degree of cold work and of the heating temperature on the grain size has been investigated for tin by Czochralski (*Int. Zeit. Metall.* 8, 36 (1916)), for copper by Rassow and Velde (*Z. Metallk.* 12, 369 (1920)) and for iron by Oberhoffer (*Stahl u. Eisen* (1919), p. 1061). Figure 66 gives the relations for iron. As a measure of the degree of work the percentage of decrease in height on compressing a prism 1.6 cm. high is used. The temperature at which the increase in grain size becomes perceptible increases with decreasing degree of work from 380 – 480° . With tin this relationship is reversed. The temperature of rapid increase of the grain size in iron increases with increasing degree of work. The grain size measure-

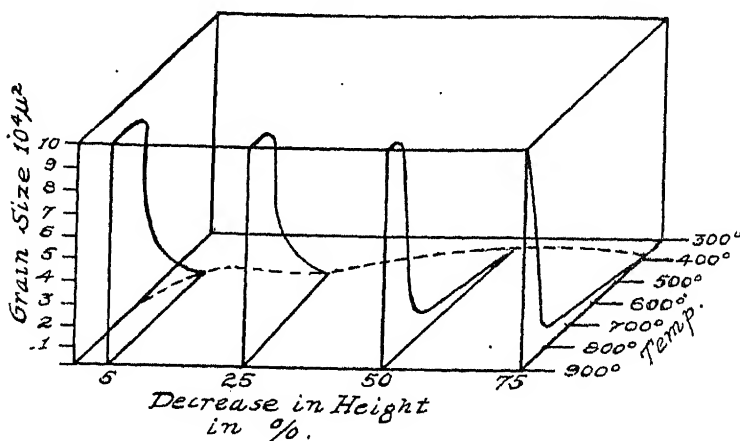


FIG. 66

ments may be made after an hour since after this period of time there is no further change of the grain size.

G. Masing (*Z. Metallk.* 12, 479 (1920) and 13, 425 (1921)) has found that a slight deformation following a greater one develops a much larger grain than does a strong deformation. The slight deformation may follow the stronger deformation at once or after a partial recrystallization.

(b) Explanation of recrystallization. The basic hypothesis is the following:

Two crystals in contact may only be in equilibrium if crystallographically equivalent lattice planes of the two crystals form the plane of contact, i.e. if the two space lattices of the crystals in contact form a single space lattice or if the plane of contact is a twinning plane.

If one or the other of these conditions is not fulfilled and if the

temperature is raised to that where there is an appreciable freedom of the atoms in the lattice, new lattice planes are formed with intermediate orientation to the plane of contact, that is, recrystallization occurs. Since it is extraordinarily improbable that at the contact of two crystals the lattice planes of one should fall in a plane with those of the other, and therefore the two crystals form a single space lattice, recrystallization practically always occurs if there is actual contact of two crystals. The basic hypothesis is accordingly a result of the atomistic structure of the crystals.

The phenomenon of twin formation shows that the contact of two crystals in a common symmetry plane, the twinning plane, does not disturb the equilibrium. The twinning plane does not result from the accidental coming together of two growing crystals but is preserved by the growing of two crystals, since the equilibrium of the two is not disturbed. On this basis we would expect that twinning would occur not infrequently in recrystallization. Its frequency is very different for different metals since the tendency to twin formation depends on the nature of the substance.

It follows from the basic hypothesis that a certain number of crystals actually in contact are transformed into one on reaching a high temperature. This process, however, is hindered by the presence of lamellae of interstitial substance.

The presence of an interstitial substance between the crystallites of so-called pure metals may be considered as an experimental fact. The purer the metal the finer are the lines of the polygonal pattern on a suitably etched surface. In the lamellae separating the crystallites, whose intersections with the surface are fine lines, the non-isomorphous impurities are thrown out by crystallization. If these are to be avoided unigranular metal fibres of considerable size must be prepared.

If a solution of lead acetate and nitric acid is allowed to act on lead, the piece slowly falls apart into its crystallites, since the interstitial substance is more rapidly dissolved than the crystallites. (Thiel, *Marburger Sitzungsberichte* (1920), No. 1, p. 1.)

If we consider recrystallization from the standpoint of our hypothesis we may explain the following facts:

1. After permanent deformation recrystallization takes place with certainty while in undeformed pieces, resulting from a melt, no recrystallization takes place by the same thermal treatment. By deformation the covering of interstitial substance around the crystals is broken and direct contact of the crystallite particles occurs. Thereby the conditions for recrystallization are met. In the undeformed piece the direct contact of crystals is not present and therefore, by heating, a change in the grain size cannot be brought about so long as direct contact does not occur.

2. Only infrequently are twinned crystallites found in cast pieces, but they occur frequently in the recrystallization of previously cold worked metal pieces. According to our hypothesis twin formation

is quite possible here since at the twinning plane equilibrium exists between the two crystals in contact. The ability for twin formation depends also on the nature of the substance. Therefore a frequent occurrence of twinning on recrystallization is to be expected only in metals which have a tendency for twin formation.

The very frequent occurrence of twinned crystallites in recrystallized copper is emphasized by all observers; it is even stated that all the crystallites are twinned, while in cast pieces of copper twinning is seldom found (see Figs. 60 and 61). Also with the solid solutions of Cu with Sn (13.6% Sn) and with 2% Au (Portevin, *Rev. d. met.* 10, 682 (1910) Figs. 9 and 34) many twins occur after recrystallization. According to Robin lightly rolled tin after recrystallization consists of pure twins while in drastically rolled tin no twins are found. Also in recrystallized lead Robin not infrequently found twins; on the other hand he found none in recrystallized Zn, Al and Fe. What special conditions are favorable to twin formation and which unfavorable to it are not known.

3. The size of the grains in iron increases with the temperature up to the transition point of α into β Fe; then the grain size of the β iron decreases slightly with increasing temperature until the transition temperature of β iron (906°) is exceeded when the grain size decreases very greatly with increasing temperature. In a metal which like Cu or Au, has no transition points, the size of the grain after recrystallization constantly increases with the temperature as in α Fe. γ Fe forms from β with volume decrease. Accordingly when crystallization centers of γ Fe form in β Fe, vacuoles form in the interstitial substance and if in β and γ Fe the thickness of the interstitial layer is the same, the grain size in γ iron will be very much less than in β iron at the same temperature. In fact the grain size in γ iron at 906° is about 10-30 times less than in β iron. The grain size of γ Fe is so small since by the volume decrease of the transition $\beta \rightarrow \gamma$ Fe the probability of contact is less and therefore the conditions for the formation of larger grains are less likely to be met.

4. Le Chatelier and Robin have found that in the folds of rolled plates of Fe, Sn, Zn, Al, Pb and Cu, the grain is much smaller than in the neighborhood of the fold. In the case of iron the recrystallized grains at first increase with increasing deformation but decrease with a large degree of deformation. (Figs. 62 and 63.)

These observations may be explained in the following way on the basis of our hypothesis.

By bending the fold fine cracks are formed in the plate whose distance apart determines the size of the grain in the fold after recrystallization. Since such cracks will form in all metals, the decrease of the grain size by previous folding is a general phenomenon. That bending metal causes cracks which are not closed in recrystallization is known from F. Credner's observation (*Z. physik. Chem.* 82, 457 (1913)) that the electrical resistance of drawn wire returns after

recrystallization to its original value while the resistance of wire bent over a sharp corner does not decrease again to its original value after recrystallization.

The abnormally small grains in the peripheral part of a Brinell impression in Fe can be traced not only to crack formation but also to the formation of many spaces as a result of the so-called simple displacement. The density of a metal in whose deformation lamellae are formed in a twinning position to the glide plane, decreases as a result of the deformation since if two such lamellae interpenetrate canals are formed at the places of intersection. With the formation of these space canals the probability of contact for the formation of new crystallites decreases. The abnormal relation of the grain size after recrystallization to the amount of deformation of iron may accordingly be understood. Whether these abnormal relations of the grain size occur only with metals whose densities are appreciably lowered by drawing into wire is still an open question. If that is not the case the abnormal relation found for iron must also occur for other metals whose densities are not changed by drawing into wire, and must be a result of the formation of cracks by great deformation and the abnormal relation of the grain size to the amount of deformation be occasioned by them. The kind of previous deformation has an influence on the grain size after recrystallization since the contact of the resulting fragments and thereby the later division of the interstitial substance may be changed.

5. The importance for recrystallization of the contact of crystallites that is caused by the rupture of the interstitial substance on small deformation in a metal piece is demonstrated by the following experiment of Czochralski (*Inter. Z. Metallog.* 8, 1 (1916)). If a rolled tin plate is allowed to recrystallize a quite small grain results. If now the plate is bent in a plane that falls in the plate and exposed to the temperature of the first recrystallization the grain grows most where there is greatest bending, while in the neutral fibres it remains unchanged. By the bending new direct contacts of the grains are formed up to the neutral fibre and these new contacts occasion the grain growth.

6. The adhesion of two pieces of metal with pure flat surfaces on pressing together is allied with recrystallization. Two pieces of lead with fresh surfaces can be welded together at room temperature by a strong pressure of the hand so that the piece in a tensile test does not break at the original surface of separation but at another place. With other metals a high temperature is necessary for welding, that for copper as well as for gold being about 400° according to Spring (*Z. physik. Chem.* 15, 65 (1894)). If two freshly turned tin cylinders are pressed together with a vise and heated in a stream of hydrogen to 150° they are cemented together in a few places. In these places crystallites are formed so that if the pieces are now separated these crystallites appear to have been a part of both pieces.

7. Electrolytic copper which consists of large similarly oriented crystals, breaks down on heating into many small unoriented crystals. The crystallites resulting at 20° are in contact with each other in an irregular manner which are the conditions for recrystallization. This can, however, only occur by raising the temperature.

8. Since recrystallization consists in regrouping of atoms in their space lattices, there is a possibility of occluded gases being evolved during recrystallization (*Z. anorg. Chem.* 114, 278 (1920)). If soft copper wire is drawn from 25 to 0.2 mm. diameter and heated in a vacuum with slowly increasing temperature, the most gas per unit time is given off between 200 and 300° . Electrolytic iron rolled from 6 mm. to 0.07 mm. thick gives off the most gas per unit time between

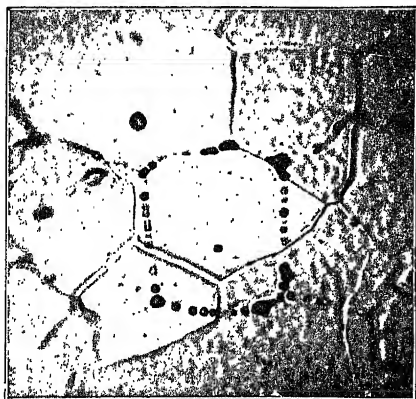


FIG. 67. NICKEL

Polished surface heated $\frac{1}{2}$ hr. at 1300° in a stream of H_2 . Air etched. $\times 500$

500 and 600° . The rate of gas evolution is accordingly the greatest at the temperatures where the properties of hard metals by slow heating change most rapidly to those of soft metals.

9. At high temperatures, where the crystallites become so soft that they are deformed by the surface tension, breaks in the interstitial layers may form as a result of such deformation. These breaks result in new contacts between the crystallites so that one crystallite may grow at the expense of the other. Also with sufficient softness of the crystallites and the interstitial substance this latter shrinks whereby, out of its lamellae, fibres or drops are formed. These form a network corresponding to the outline of original crystallites and remain after recrystallization. Fig. 67 shows a section of a repeatedly melted Ni-rod which has been heated one-half hour at 1300° in H_2 .

10. The displacement of the crystallite boundaries has been investi-

gated by Carpenter and Elam (*Engineering* 60, 385 (1920)) and by Vogel (*Z. anorg. Chem.* 126, 1 (1923)). The occurrence of two or more polyhedral networks has been observed in iron by Osmond,

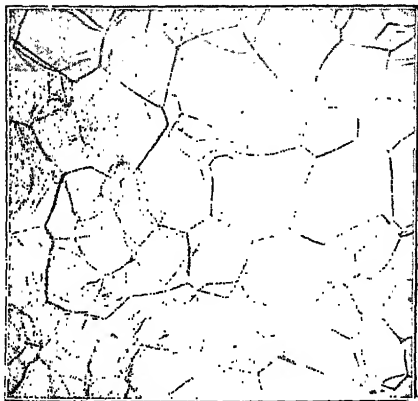


FIG. 68. CADMIUM
Cast on a glass plate, unetched. $\times 100$



FIG. 69. ZINC
Cast on a glass plate, unetched. $\times 50$

Kroll and Ewen. The formation of the most prominent network has been ascribed to crystallization from the melt, the second to the transition of γ into β iron and the third to that of β into α iron. Now, however, double and fourfold networks are observed in metals which lack these transitions. Fig. 68 shows such a network in cadmium

cast on a glass plate and Fig. 69 such a network in zinc. The second finer network has apparently formed after recrystallization since at many places the interstitial substance is lacking at the boundaries of the original crystallites; accordingly a contact exists at sufficiently high temperature. By dendritic crystallization indented crystallite boundaries form but by quick crystallization smooth boundary lines result. Fig. 70 shows the networks in lead cast on glass, one with indented boundaries, the other with straight. The glide lines formed by slight deformation, Fig. 71, show that the indented network formed first and went over by boundary migration into the smooth and that this latter network corresponds to the outline of the crystallites.

11. In crystallite conglomerates the combination of two crystallites is prevented by the interstitial substance and takes place only after cold working. Various methods lead to different temperatures for the beginning of recrystallization.

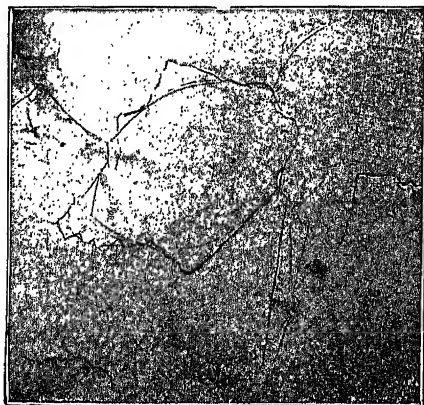


FIG. 70. LEAD

Cast on a glass plate, unetched. $\times 50$

In a loose powder, kept in constant motion by a stirrer, combination should occur at a lower temperature than in conglomerates with fixed particles since in loose powder the probability of favorable contact is incomparably greater than in conglomerates with fixed particles.

The temperature of the beginning of combination of the particles of a powder may be easily determined by heating the powder in which the stirrer rotates and noting the temperature at which the stirrer stops. (Tammann and Mansuri, *Z. anorg Chem.* 126, 119 (1923).) In Table 12 the temperatures at which the stirrer stopped are shown in comparison to the temperatures of beginning of recrystallization as determined by other means.

TABLE 12

	Temp. of Decrease of Electrical Resistance	Temp. at which Stirrer Stops	Temp. of Crystal Growth in a Pressed Powder	Temp. of the Change of Structure
Au	100°	—	—	—
Ag	130°–230°	140°	<578°	—
Cu	160°–200°	145°	720°	200°
Ni	<220°	—	1100°	350°
Fe	<185°	148°	1100°	—
Al	—	140°	>630°	—
Zn	—	140°	>360°	75°

The temperature of the beginning of the decrease of electrical resistance (F. Credner, *Z. physik. Chem.* 82, 476 (1913)) of a hard drawn wire gives a temperature for the beginning of recrystallization and therefore for the beginning of motion of the atoms in a lattice only slightly higher than that at which the stirrer stops. With the stopping

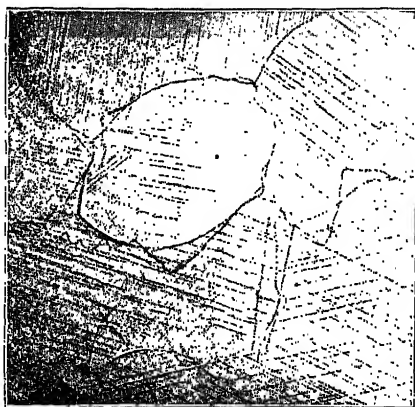


FIG. 71

Same location as in Fig. 70. Slip lines formed through slight bending. $\times 50$

temperature of the stirrer in Ag and Cu powder there coincides a sharp chemical reaction limit in the solid solutions of Au with Ag or Cu. The microscopic determination of the temperature of change of structure after cold working is very insensitive. In pressed pieces of metal powders whose parts are covered with oxide, the crystal growth takes place at very high temperatures. (F. Sauerwald, *Z. anorg. Chem.* 122, 277 (1922).) The metal powders used for the determination of the stopping temperature of a stirrer were also covered with oxide but this is in part rubbed off by the motion.

12. The roughening of polished metallic surfaces at high temperatures.

The polish on an Ag sheet begins to become matted in a stream of hydrogen in 1 to 2 hours at 110° and at 300° the formerly polished surface is rough; the surfaces of the individual crystallites are no longer planes but cups. If strips of silver foil are heated at the end in a bunsen flame so that part of the end melts the larger crystallites are entirely bright. After the bright zone there follows a very rough zone in which dendritic crystallites have grown out in the original surface. With decreasing temperature the size of these forms decreases.

With copper the temperature of matting of a polished surface is higher than with silver, that with Ni being still higher. With both these metals the presence of a small amount of oxygen in the hydrogen has a great influence. Polished nickel retains its lustre at 400° in pure hydrogen but loses it at 300° if the H_2 contains some oxygen.

The first matting of polished Ag is a result of recrystallization. At higher temperatures where the metal is softer the tension converts the plane surfaces of the crystallites into cups and these finally go over to dendritic forms.

13. Grain Growth in Mixtures of Crystals and Melt.

The phenomenon of small crystals in a saturated solution growing together to a continuous crystalline mass is not to be confused with that of recrystallization in conglomerates. The former kind of crystallization may be traced to the fact that the solubility of small crystals is greater than that of larger crystals. We have, however, no means of determining whether this explanation of the phenomenon is correct or not. It has neither been proved whether the welding of individual crystals takes place at constant temperature in a saturated solution nor has it been determined whether the difference in the solubility of crystals of different sizes is sufficient to explain the diffusion relations necessary for this phenomenon. The welding of damp crystal masses which fluctuate in temperature and contain saturated solution can certainly be due only in a very small degree to the difference of solubility of different grain sizes since one observes that welding takes place more rapidly the greater the absolute temperature coefficient of solubility, $\frac{dc}{dt}$, and the greater and more numerous the temperature fluctuations, Δt in the mixture of crystals and saturated solutions. The velocity v with which the loose crystals grow together when in contact with the saturated solution is given by the relation $v = k.n.\Delta t \frac{dc}{dt}$. Here k is a constant and n the number of temperature fluctuations in unit time.

From this we conclude that the phenomenon is brought about by temperature fluctuations. In order to study the effect of the difference of solubility of large and small crystals on v we must reduce Δt to a vanishingly small value.

To learn the influence of $\frac{dc}{dt}$ on the cementing, three saturated solutions with quite different values of $\frac{dc}{dt}$ were placed in well closed flasks in contact with their solid phases as loose powders and subjected to fluctuations of room temperature that amounted to 7° in 24 hours. Corresponding to the series of $\frac{dc}{dt}$ values, for naphthaline in alcohol 0.95, for potassium alum in water 0.14, and lead chloride in water 0.016, we find that the original loose naphthaline crystals are already so well cemented together after 24 hours that the mass cannot be separated by shaking the flask. The same takes place for the alum crystals after four times 24 hours and with lead chloride does not take place after a month, although a lead chloride crust has formed on the flask wall.

Similar phenomena are observed in metallic melts. If alloys of two or more components are held for a long time in the temperature range in which they are partially molten a very great growth of the primary crystals is to be observed.

14. The Velocity of Recrystallization and the Recurrence of the Natural Elastic Properties.

It is very difficult to measure the velocity of recrystallization by the amount of recrystallized metal per unit of time. It is easier to obtain a picture of the velocity of this process in relation to the temperature and time if we follow the recurrence of the original properties which have been changed by cold work. By this means it is proved that after each temperature increase the recurrence of the original properties sets in with the noticeable velocity and then, however, it very soon slows down and even at higher temperatures after an original rapid run it soon becomes inappreciable. The process begins at quite low temperatures which apparently correspond to the temperatures where the motion of the atoms in the lattice becomes appreciable. With increasing melting point the temperature of recrystallization also increases. With lead this temperature is below ordinary temperature. Hence lead cannot be permanently hardened by cold work. Therefore, if a permanent change of properties takes place the working temperature must not be in the temperature zone of rapid recrystallization.

For low carbon steel, which as rolled wire of 7 mm., was reduced to 2.7 mm. in 5 passes, the degree of working in % being accordingly

$$\frac{\left(\frac{7}{2}\right)^2 - \left(\frac{2.7}{2}\right)^2}{\left(\frac{7}{2}\right)^2} \times 100 = 85\%.$$

P. Goerens found the tensile strengths and elongations shown in Fig. 72. These are for the wire in the cold state after heating to a definite temperature for various times.

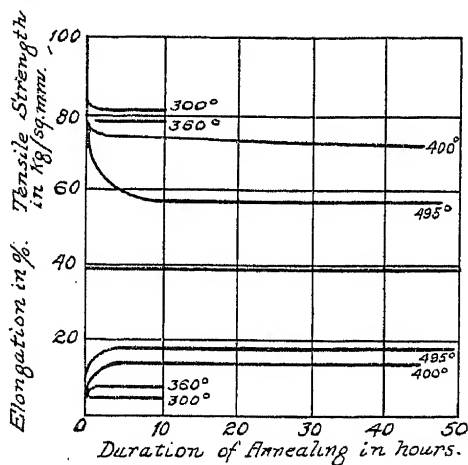


FIG. 72

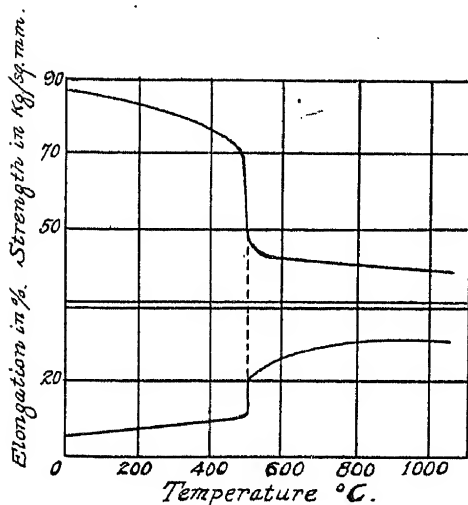


FIG. 73

We see from this that for every temperature of heating, the initial velocity of the change in tensile strength and elongation is very great; however, it soon reaches a practically constant condition. The nature of this return of the material to its natural state cannot be reconciled

with the assumption of the formation of a new iron phase by the working and its transition into ordinary iron by raising the temperature.

Entirely similar relations are met for the recurrence of the natural electrical resistance of drawn wire by heating.

The relation to the temperature of the end value of the strength and elongation reached at a definite temperature is summarized in Fig. 73. (Goerens, *Ferrum* 10, 229 (1913).)

15. Is the Deformation of a Crystallite Conglomerate caused by Transient Melting.

We very frequently find the viewpoint taken that the flow of glacier ice may be traced to transient melting and resulting crystallization. It has been sought to carry these conclusions over to the deformation of all crystallite conglomerates. Now we have already seen that the crystallites of conglomerates have a great ability for deformation by the formation of glide planes. Accordingly the assumption of a transient melting to explain the phenomenon of flow is quite superfluous. Still the questions to be answered are whether or not the displacement along the glide planes takes place by transient melting, and under what conditions it can occur. To this end we will first consider the action of strain on a crystal in contact with its melt.

(a) The action of strain on a crystal in contact with its melt. We will consider a crystal that is surrounded by its melt under a compressive strain in a definite direction. Since the strength of an anisotropic body is very small at its melting point, this strain must be very small, probably not more than 100 kg. per square centimeter, if the body is not to be permanently deformed by the strain. A definite hydrostatic pressure p occurs in the melt and the entire system is brought to a temperature T corresponding to this pressure. The temperature T is so chosen that at the pressure p equilibrium exists between the crystals and its melt before the application of the strain. By the application of the strain the equilibrium is disturbed, and since the thermodynamic potential of the crystals in this state is greater than in the natural state, in which only the hydrostatic pressure of the melt is active, the crystals will grow at the places of least strain at the expense of those of greatest strain. Accordingly by the application of a compressive strain only a recrystallization occurs. If the crystal is compressed by means of two wires on two parallel surfaces, the wires will approach each other very slowly by means of this recrystallization since at the compressed place the crystal melts and at the strain-free places crystals deposit. The necessary conditions for this recrystallization by pressure are, however, that the temperature and hydrostatic pressure of the melt fall at a point on the equilibrium curve of the crystals with their liquid.

The question is still to be answered, whether or not melting can occur at temperatures lower than that of the equilibrium tempera-

ture that corresponds to the hydrostatic pressure P . This question is no longer in the domain of equilibrium theory, and therefore, the application of the second law of thermodynamics in its regular form leads to incorrect results. We may now very well ask the question what will happen if a crystalline substance is so pressed that it or its eventually formed melt may escape. If the pressure is applied by means of a tight fitting piston melting will take place when the pressure of the equilibrium curve of the crystals is exceeded, which can be deduced from the second law of thermodynamics; if, however, the piston is not tight fitting the pressure changes are no longer reversible and the second law can no longer be applied. What will take place in this case can only be learned with certainty from experiment.

(b) **The rate of extrusion of crystalline substances.** The Process: To measure the rate of extrusion it must be so conducted that the pressure measured is that actually present in the layer flowing. Further it is necessary for the realization of stationary rates of flow that the pressure be held constant and therefore, care must be taken not to exert a counter pressure on the flow by obstructions. These conditions for obtaining stationary rates of flow have been taken into account in the following process.

The substance to be investigated is placed in a cylindrical vessel A, and the cylindrical pin F presses on it. A cross section is shown in Fig. 74. This arrangement corresponds to the condition that the extruding layer, which lies under the basal plane of the pressure pin is under a definitely measurable pressure which is exerted on the upper surface of the pressure pin by a rod E.

The orifice is a ring-shaped cylinder of 0.5 mm. height, through which the crystalline substance is pressed as a thin walled tube. If this tube is extruded to the upper widening of the pressure pin it breaks off. Gradually the broken pieces of this tube accumulate in the space between the cylinder wall and the narrow part of the pressure pin without interposing a noteworthy resistance to further flow.

If a pressure pin of the form described is replaced with a solid cylinder the rate of extrusion at constant temperature and constant pressure decreases rapidly from minute to minute.

Increase of the rate of extrusion is obtained by using a pressure pin with a cone shaped bottom. The same result can be obtained by enlarging the ring-shaped orifice.

(c) **The extrusion velocity of ice and its melting curve.** The determinations of rates of extrusion show that flow begins at low pressures and increases progressively up to a certain pressure, which depends on the temperature, when a sudden acceleration of the extrusion takes place. When this pressure is reached the lever which transmits the pressure plunges with great velocity to its support in the frame of the pressure apparatus. By lowering the frame 9 mm. per second the lever end still follows it while at a somewhat lower

pressure the greatest lowering of the lever only reaches $\frac{1}{60}$ of this amount. With increasing pressure at constant temperature the rate of extrusion of ice increases rapidly and then at a certain pressure depending on the temperature increases discontinuously to values that are not measurable with the lever arrangement. The observer gets the impression that we are dealing here with a transition from a strongly hindered movement of the pressure pin to a practically free movement of the same through the ice mass. The sudden increase of this motion is comparable with the transition of the strongly increasing tension of a metal cylinder above its elastic limit to the free motion of the stretching load after the break.

The agreement of the velocities measured immediately after one

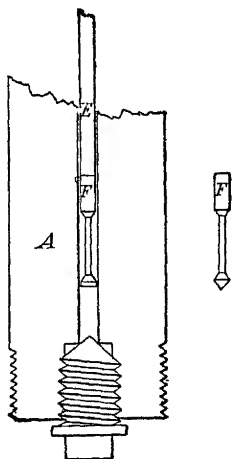


FIG. 74

another shows that the pressure pin moves forward with a stationary velocity in ice at a definite temperature and pressure. If the pressure is lowered, however, the pressure pin sinks at the same pressure always with less velocity than previously with increasing pressure. This phenomenon is entirely general and is shown by all the substances investigated including amorphous substances. With increasing pressures we move along an extrusion curve which lies above that on which we move with falling pressure. In general the rates of extrusion that are determined with increasing pressure have the tendency to fluctuate with the time while the rates of flow determined at falling pressures have a tendency to increase with the time.

The stationary velocity is influenced in an extraordinary degree by both the temperature and pressure. These results are summarized in Table 13.

A pressure increase of 100 kg. brings about as a rule an increase

of rate to double that present. At low pressures the increase is still greater. Also the temperature influence at constant pressure is extraordinarily great, a temperature rise from -15.7° to -5.7° is enough to increase the velocity to 20-100 times its value. With decreasing temperature the influence of temperature is somewhat less. The great dependence of the viscosity of ice on the temperature reminds one of a supercooled liquid in the neighborhood of the temperature interval of softening, concerning which a few measurements have been made (*Z. physik. Chem.* 28, 17 (1899)).

TABLE 13

p kg.	$t^{\circ} = -5.7$	-10.7	-15.7	-21.7
100.....	0.9	0.03	—	—
200.....	4.1	0.3	—	—
300.....	11.8	2.0	0.1	—
400.....	22.5	4.1	0.3	0.15
500.....	49.5	8.3	1.5	0.3
600.....	95.0	19.0	5.1	0.5
700.....	—	34.0	12.6	2.5
800.....	—	60.0	22.0	7.0
900.....	—	101.0	—	13.5
1000.....	—	170.0	—	20.5
1100.....	—	—	—	30.0
1200.....	—	—	—	53.0
1300.....	—	—	—	65.0

The pressure at which a discontinuous increase in the rate of extrusion takes place at various temperatures is as follows:

TABLE 14

t°	Pressure at which the Lever Plunges kg./sq. cm.	Highest Pressure at which a Stationary Velocity Can Be Measured	Equilibrium Pressure in kg./sq. cm.*	Δ
-5.7	665	642	678	+ 13
-10.7	1130	1116	1225	+ 95
-15.7	1729	1611	1681	— 14
-21.7	2100	2000	2170	+ 70
-27.6	2240	2220	—	—

* *Ann. Phys.* 2, 1 (1900).

If we compare the pressure at which the lever plunges with the equilibrium pressure of ice and water, as determined by an entirely different method, and take into account that a small temperature error causes a very considerable pressure change and that the measurement of pressure on the lever apparatus is less exact than that of the equilibrium pressure, since at the fulcrum of the lever a not considerable frictional resistance must be overcome, we may say that the lever plunges at the melting pressure, and that melting first takes place if the pressure of the equilibrium curve is exceeded.

(d) The melting of a substance by isothermal pressure increase. With substances which melt with increase in volume, the pressure must be raised very high to be above the equilibrium pressure. If we represent, as in Fig. 75, the equilibrium curve of a crystal with its melt by the curve with a maximum, T_m the field of existence of the crystallized substance on the pressure-temperature plane is bounded completely by the T and p axes and the equilibrium curve. If now a substance is to be melted by pressure increase at a temperature below its making point T_o , the equilibrium curve must be exceeded at constant temperature as the experiment with ice has shown. This will occur at the temperature T_o first at the point a . Now, however, the maximum melting point T_m for most substances lies at very high pressures, the point "a" accordingly at still higher pressures. With Glauber's salt, the pressure p_m is exceptionally low, being only 495 kg./sq. cm. Therefore, it is possible to melt Glauber's salt by pressure increase below the temperature T_o . At 32° ($T_o = 32.6 + 273^\circ$) the

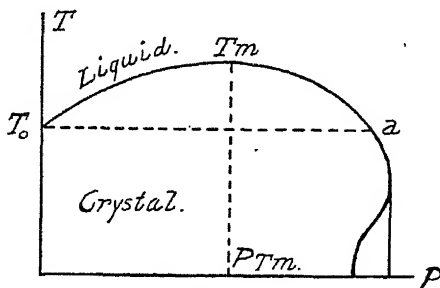


FIG. 75

melting of Glauber's salt takes place at 2000 kg./cm. and with lowering temperature it takes place with always increasing pressure. Between T_o and T_m ($T_m = 32.8^\circ + 273^\circ$) liquid Glauber's salt at first crystallizes on an increase of pressure and then at higher pressure again melts. Above T_m liquid Glauber's salt cannot be crystallized by a pressure increase.

With most substances T_m lies at pressures of at least 10,000 kg., with metals it lies at still higher pressures. The assumption that with deformations which can be brought about below 1000 kg., the substances and especially the metals are transiently melted, and that flowing of metals may be traced to partial transient melting is entirely untenable. Also as we have seen such an assumption is superfluous since the formation of glide planes in the plastic metals confers sufficient mobility. The conditions under which melting occurs are shown by the equilibrium diagram. We may, therefore, make no assumptions of melting that are contradictory to the equilibrium diagram which gives the course and position of the equilibrium curves on the p, T plane. Until recently we had only a very incomplete idea of that

part of the equilibrium diagram in which the solid anisotropic state plays the principal rôle, and hence arbitrary assumptions in regard to transient melting or the assumption of modifications of anisotropic bodies have been made in order to explain the phenomenon of flow.

(e) The rate of extrusion of several metals. The rate of extrusion of several metals was determined in the above described way (Werigin Lewkojeff u. Tammann, *Ann. Phys.* 10, 647 (1903)). Since the values of this velocity at the same temperature and pressure are greatly different, quantitative determinations of the velocity under definite conditions cannot be made; we may, however, arrange the metals in a series in which the velocity of extrusion decreases very greatly from left to right. This series for 0-100° and 1-1000 kg. at the same temperature and pressure is:

K, Na, Pb, Tl, Sn, Bi, Cd, Zn, Sb.

Further at the same pressure a 10° increase in temperature nearly doubles the value of extrusion velocity through the same opening. This is shown by the following measurements for tin.

TABLE 15
PRESSURE 1000 KG. PER SQ. CM.

Temp.	Scale Divisions per Minute			Average	
10.0°.....	0.2	0.2	0.2	0.2	0.0
20.0°.....	0.4	0.4	0.5	0.4	0.0
32.0°.....	0.7	1.0	0.9	0.9	0.1
41.8°.....	1.6	1.5	1.7	1.6	0.1
51.2°.....	4.0	3.8	3.6	3.8	0.1
60.5°.....	8.3	7.7	7.7	7.9	0.3
70.4°.....	14.3	13.2	14.9	14.1	0.6
83.2°.....	32.0	33.6	31.8	32.5	0.8
90.6°.....	59.7	55.5	54.3	56.5	2.1
100.3°.....	107.6	89.2	96.0	97.6	6.6
110.5°.....	206	178	201	195	11.3
120.6°.....	—	362	—	362	—
131.4°.....	—	584	—	584	—

For ice (Table 13) we found between —20° and 0° a considerably more rapid increase of the rate of extrusion with increase in temperature. It also appears that the increase in rate of extrusion of metals in the neighborhood of their melting curve is considerably greater than at lower temperatures.

The rate of extrusion of a crystalline body may be assumed to be proportional to the friction on the gliding surfaces, if the number of glide surfaces in an equal amount of extruded material is not changed by temperature and pressure; if this number increases, the rate of extrusion will increase. It is very possible, that for metals the simple law of rate of extrusion due to temperature change, i.e. doubling the rate of extrusion for every 10° temperature rise, proves correct since within a certain temperature range and a given distance from the melting point the number of glide planes is independent of

the temperature. If that is the case the rule for the temperature relation of the rate of extrusion will hold also for the temperature relation of the friction on the glide surface.

(f) **The melting curves of several metals.** The melting curves of several metals were first determined by the author by two methods. For K and Na the equilibrium pressure of the crystals and their melt at constant temperature was determined by observing the pressure and volume changes that occurred in a mixture of crystals and their melt up to pressures of 3000 kg. (*Kristallisieren und Schmelzen*, pp. 193 and 245-248.) For Bi and Sn the cooling curves of the metals were taken at practically constant pressure, and from the change of the arrest temperature in the cooling curves of the molten metal the influence of pressures up to 3000 kg. on the melting point obtained. (*Z. anorg. Chem.* 40, 54 (1904).) Later Bridgman (*Proc. Amer. Acad. Arts. Sci.* 47, 393 (1911)), by the first method, accurately determined the melting curve of mercury up to 12,000 kg. and Johnston and Adams (*Z. anorg. Chem.* 72, 11 (1911)), by the second method, those of Sn, Cd, Pb and Bi up to 2000 atm.

The relation of the melting point to the pressure can as a rule be represented by an equation of the simplest form.

$$t_p = t_p = 0 + ap - bp^2.$$

The coefficient A is equal to $\frac{dt}{dp} = \frac{\Delta v T}{42.7 \delta_p}$ where Δv is the volume change on melting 1 gram, δ_p the heat of fusion in calories, T the absolute temperature and 42.7 the mechanical heat equivalent of 1 Cal. in kg./cm. In the following table the values found for a and b as well as those calculated for a are collected. We see that a pressure of 1000 kg. increases the melting point of the metals with the exception of K and Na only 3-8° and that only with Bi, which expands on crystallizing, does a lowering of the melting point occur. The maximum melting point of metals T_m (Fig. 75) must be at very high pressure since the coefficient b is very small.

16. The Changes of Elastic Properties by Deformation.

The modulus of elasticity of hard and of soft (annealed) material is different according to Wertheim (*Pogg. Ann.* 78, 391 (1849)) and this difference changes with the nature of the material in a very important way.

TABLE 17

	Hard kg./sq. cm.	Annealed kg./sq. cm.	Difference in %
Cu	12,449	10,519	18.30
Ag	7,357	7,140	3.00
Au	8,131	5,584	45.60
Pb	1,883	1,727	9.00
Fe	20,869	20,794	0.30

That the modulus of elasticity of iron does not appreciably change with the degree of work has recently been confirmed by P. Goerens (*Journ. of the Iron and Steel Inst.* 3, 320 (1911)). In Fig. 76 are plotted the elastic limits of iron rods, as found from the tension elongation diagram, in relation to the percentage of working (p. 97). While the elastic limit increases greatly the modulus of elasticity remains practically unchanged. The numbers on the curves give the carbon content of the steel.

How complex the influence of cold working may be on the individual elastic properties may be seen from the following. The difference between the "bendability" of a hard and soft wire is recognized. This can be compared to the difference in bending a rolled and an unrolled

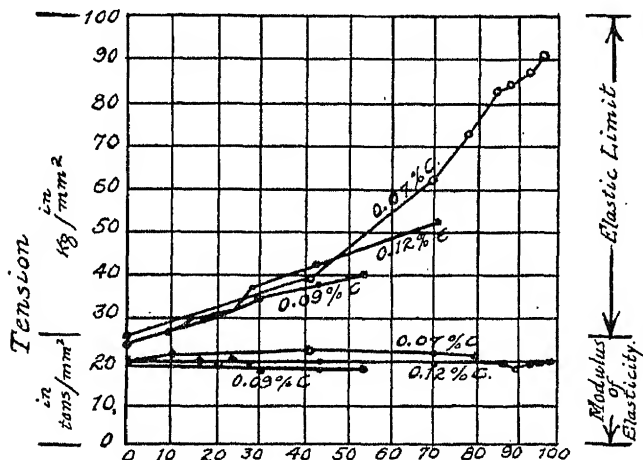


FIG. 76

sheet of paper. If in the rolled paper strong tensions are set up in the direction of the tube axis the resistance to bending is still further raised.

If rods of Al or Cu are twisted above their elastic limit and then twisted in the opposite direction, according to P. Ludwick (*Z. d. Oesterr. Ing. u. Archt-Vcr.* (1916), No. 42) the restoring force for the same angle of tension is considerably smaller for the opposite torsion than the force after the first torsion. By the first permanent deformation numerous glide planes have been formed along which the opposite displacement, brought about by reversing the force, naturally takes place with less force than at the conclusion of the first rotation where the force must still form new glide planes. With the increase of the opposite rotation the number of new glide planes increases and, therefore, the force again increases rapidly. By reversing its direction the force again falls.

If a wire is twisted it does not, after the removal of the force, immediately turn completely back if the elastic limit has been exceeded but a rapid return followed by a relatively slow one following an exponential law takes place, the period of elastic hysteresis. Von Wartenberg (*Verhandl. d. deutsch. phys. Ges.*, p. 113 (1918)) has shown that single crystal wires prepared by the process of Schaller (*Zeit. Electrochem.* 23, 121 (1917)) out of tungsten or by the process of Czochralski (*Z. physik. Chem.* 32, 219 (1917)) out of zinc do not show elastic hysteresis while wires out of identical materials which consist of many crystals always show elastic hysteresis. In the wires consisting of many crystals permanent deformation takes place below the elastic limit, which can be recognized microscopically by the gliding. However, the inner field of force will slowly restore the original condition. Since these displacements are lacking in single crystal wires no elastic hysteresis occurs.

17. The Relation of Technical Mechanical Properties to the Temperature.

With increasing temperature the tensile strength of metals decreases at first slowly then rapidly so that at a red heat most metals have only a very small tensile strength. Noteworthy exceptions are certain alloys of cobalt with Cr, Mo, and W, which still possess a tensile strength at a red heat such as steel has at ordinary temperatures (see p. 112, the Cobalt-Chromium alloys).

With metals in which no transformations occur the decrease of tensile strength with increasing temperature is more regular than with metals which show polymorphic transitions.

M. Rudeloff (*Mitt. d. techn. Versuchsanstalten zu Berlin* 11, Heft 6, 292 (1893)) determined the pull at different temperatures at which copper rods would greatly elongate at practically constant tension (the stretch limit). With annealed copper rods the stretch limit of 500-600 kg./sq. cm. at 20° decreases only slowly to 300-500 kg./sq. cm. at 400°. On the other hand with hard drawn copper wire this decrease is very pronounced; the stretch limit falls from 3200 kg./sq. cm. at 20° to 2400 kg./sq. cm. at 200° and to 300 kg./sq. cm. at 400°. At 400-500° the great difference in the stretch limit of hard-drawn and annealed copper disappears.

If the decrease of the tensile strength and the falling of the stretch limit occur regularly with increasing temperature, as with annealed copper, the force necessary to develop glide planes obviously decreases regularly. The elongation at the stretch limit depends on the number of glide surfaces. Accordingly if the elongation at the stretch limit increases with increasing temperature, we may assume that the ability to form glide planes (see p. 72). increases with increasing temperature.

That with increasing temperature the stretching limit of a hard

metal falls to that of the annealed, is obviously to be traced to the process of recrystallization by which the metal becomes soft in the temperature interval of the decrease of stretching limit.

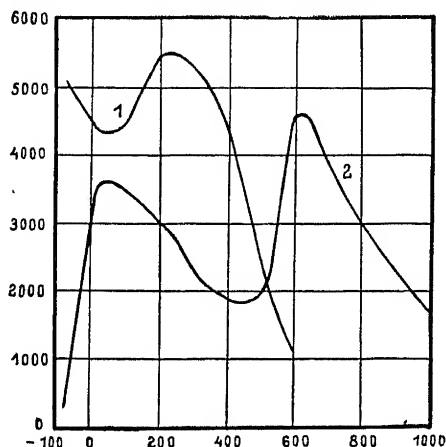


FIG. 77

1. Maximum tensile strength in kg./cm^2 .
2. Maximum work of impact in kgm/cm^2 .

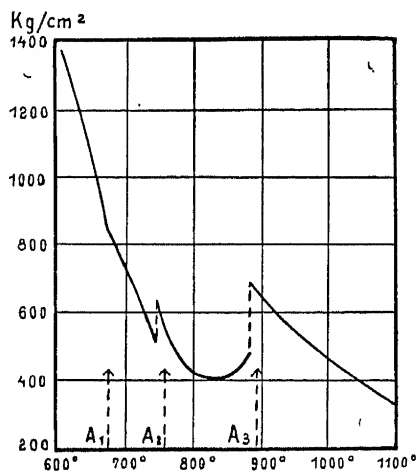


FIG. 78

Maximum tensile strength in kg./cm^2 .

The temperature relation of the tensile strength of iron is in many ways abnormal. The maximum tensile strength per unit cross-section (according to A. Martens, *Mitt. d. techn. Versuchsanstalten zu Berlin*

8, *Heft* 4, p. 189, Fig. 14 (1890)) is plotted in curve 1, Fig. 77. The minimum of the tensile strength at 20° and the maximum at 220° are characteristic of α iron. At higher temperatures still other abnormalities occur in the temperature relations of the tensile strength of iron that are obviously connected with the transition of α into β Fe and that of β Fe into γ Fe. In Fig. 78 is plotted the maximum tensile strength in relation to the temperature between 600° and 1100° according to the measurements of W. Rosenhain and J. Humfrey (*Journ. of the Iron and Steel Inst.* 219 (1913)). At the transition points A_2 and A_3 we may assume a natural discontinuous change in the maximum tensile strength. The maximum tensile strength of the iron accordingly changes discontinuously with the change in nature of the crystallites of iron.

The temperature relation of the mechanical properties changes greatly with the kind of work. The mechanical properties and their temperature relations may be very different for a rapid and for a slow action of the working force.

The work of impact which break a notched test piece serves as a measure of rapid acting momentary work (Charpy's test). If the weight of the hammer is multiplied by the difference of height between the fall and the rebound of the hammer and the product reduced to a unit of cross section at the place of breaking, this value is the specific work of impact, a measure of the momentary working of the test piece by a hammer blow. The relation of the specific work of impact to the temperature for soft steel according to Goerens and Hartel (*Z. anorg. Chem.* 81, 130 (1913)) is shown in Fig. 77, curve 2, and in curve 1 the maximum tensile strength by slowly increased load according to A. Martens. The specific work of impact decreases rapidly with decreasing temperature below 20° . The iron is brittle with respect to the action of a blow. On the other hand its tensile strength by slow loading increases with decreasing temperature. Also by heating from 20° the impact strength decreases with increasing temperature while the tensile strength increases. While, however, from 250° to 750° the tensile strength decreases strongly with increasing temperature, the work of impact increases considerably from 20° to about 600° and then decreases again. An influence of the polymorphic transitions of iron on the impact strength, such as is clearly shown on the maximum tensile strength (Fig. 78) has not been found (Fig. 77, curve 2).

The difference in behavior of soft steel with respect to suddenly and slowly applied force is to be traced to the difference of glide plane formation with different velocities of increase of the working force. If the formation of glide planes is a rapid process the curves for tensile strength 1 and impact strength 2 would run parallel to each other. At temperatures where the impact strength is especially small the time during which the blow acts is not sufficient for the formation of glide planes. Therefore the material is brittle towards

suddenly increasing loads, although its elongation and its maximum tensile strength by the action of slowly increasing forces is very considerable.

The decrease of impact strength with falling temperature is apparently a general phenomenon, since the velocity of the glide plane formation is probably very small at low temperatures. The minimum of the impact strength at 450° is, however, a phenomenon characteristic of iron which may be traced either to the fact that in the temperature interval between 350° and 500° the formation of glide planes needs a longer time than at either lower or higher temperatures, or that in this temperature interval the internal strains are especially great.

P. Ludwik (*Z. physik. Chem.* 91, 232 (1916)) determined the cross section of the impression of a cone which would be formed by a definite load in a definite time for various temperatures in various metals. If we plot the load necessary to produce an impression of a unit cross section against the absolute temperature divided by the melting point these hardness curves for Cu, Zn, Bi, Sn, and Pb have similar courses. The curves for Sb and Al cut those of the above-named metals. At the melting point the hardness of Sn and Bi is about 10 per cent. of the hardness at ordinary temperature while that of Pb is 7 per cent. and those of Zn and Cd are 2 per cent.

A substance which is especially strong in tension and compression at high temperatures is important for many purposes. A series of alloys which is characterized by these relations is that of Co-Cr. In the following table several mechanical properties of the Co-Cr alloys at 720° are collected. At 720° the elastic limit and breaking strength of an alloy with 30 per cent. Cr exceeds the values of these properties for many construction materials at 20° .

Composition of the Alloy		σ_s Elastic Limit	σ_B Breaking Strength	Elongation in % of Length of Piece	Reduction in Area in %
Cobalt	Chromium	in kg./sq. cm.			
75%	25%	2810	4490	21.0	26
70	30	4590	6510	8.6	22

18. The Volume Changes Produced in a Crystal Conglomerate by Deformation.

The conglomerates of pure metals formed from a melt and the conglomerates of a series of solid solutions consist of polyhedral grains closely packed. The planes, where these polyhedra touch, are, however, not crystallographic planes, but the geometric locus of the crystal centers from which the crystals have grown. Therefore the polyhedral surfaces have no definite orientation to the planes of the original crystal.

Since contraction generally occurs on the crystallization of metallic melts, the space is not completely filled with the polyhedra, and gaps

remain between them. As a result metals are made at first more dense by light hammering since this closes the gaps resulting from the crystallization. By drastic permanent deformation of the metal, three kinds of new gaps may form.

1. Gaps between the polyhedrons may result by displacement of parts of the crystallites.

2. Space canals must form in the polyhedrons themselves if not translation, but displacement occurs in them which the mineralogists call "simple displacement" (Fig. 33, p. 67). There is formed by this displacement a lamella in the crystal which on the application of force rotates into a twinning position whereby parts of the crystal are displaced without losing their continuity. Thereby a space open to the outside (Fig. 79) or a space inside of the crystal (Fig. 80) may form. The two figures are cross sections of crystals. The rotated lamellæ are cross hatched, the space blackened.

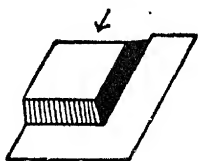


FIG. 79

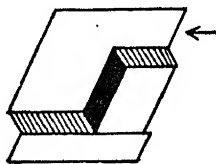


FIG. 80

Such canal formation can be easily observed by working transparent crystals and G. Rose (*Abhandl. d. Akad. Wiss. Berlin* (1868), p. 57), the discoverer of these canals, has described the formation of the canals in calcite crystals to such an extent that the crystal is rendered cloudy.

3. A loosening of the cohesion and therewith a lowering of density can occur by the formation of glide surfaces, whether a simple displacement or translation takes place on these glide surfaces.

The density of a metallic casting is accordingly dependent on its deformation in the following way. By slight deformation, light rolling, hammering, etc., the density first increases since the gaps between the crystals are closed. By greater deformation a maximum density may be reached where the volume of the spaces closed is equal to the volume of the new ones formed. Finally by more drastic deformation, when the number of newly formed gaps begins to exceed those closed, the density decreases.

If a drastically deformed metal, e.g. a wire, is brought into the temperature range where the doubled surface tension exceeds the strength that results from glide plane formation, the lamellæ are welded together and also a part of the remaining gaps closed, and an increase in density is accordingly to be expected. We understand from this standpoint the action of the important technical processes, drawing, rolling, etc., whereby the material, after a certain series of

deformations, is made soft again by annealing. These operations close the gaps and therefore prevent cracking.

George Kahlbaum and his coworker Sturn (*Z. anorg. Chem.* 46, 217 (1905)) have made a comprehensive direct study of the change in density by the preparation of wires, the principal results of which are summarized here (see Table 18).

The mean difference in density of soft annealed and of hard cold-drawn wires amounts to 0.0164 with a mean error of density of 0.0004. The deformation by wire drawing whereby the diameter of wire is decreased 0.3 m gives a certainly detectable density decrease of 0.077 per cent.

Kahlbaum and Sturn found for soft, fully annealed metals, and hard cold drawn metals, the mean densities given in Table 19 which give the corresponding percentage differences noted.

TABLE 18

	Density		
	1	2	3
3 platinum cylinders.....	21.2137	21.3060	21.4144
Forged to bars and rolled.....	21.4314	Considerable increase 21.4194	21.4144
Cold drawn to wire of 1 mn.....	21.4136	Decrease and increase 21.4226	21.4233
Annealed 3 min.....	21.4314	Appreciable increase 21.4323	21.4324
Cold drawn to wire of 0.7 mn.....	21.4181	Decrease 21.4157	—
3 minutes annealed.....	21.4314	Increase 21.4315	21.4332
Cold drawn to wire of 0.4 mn.....	21.4142	Decrease 21.4147	21.4134
Annealed 3 min. white heat.....	21.4308	Increase 21.4310	21.4317

TABLE 19

	Soft	Hard	Decrease in Density by Working in %
Pure platinum	21.4403	21.4133	0.13
Platinum iridium	21.4938	21.4766	0.08
Gold	19.2601	19.2504	0.05
Aluminum wire	2.7030	2.6995	0.13
Aluminum sheet	2.7127	2.7107	0.07
Cadmium	8.6434	8.6379	0.06
Nickel	8.8439	8.7599	0.19 *
Piano wire	7.7970	7.7772	0.25
Silver	10.4475	10.4410	0.06
Copper	8.8317	8.8313	0.00
Tin	7.2831	7.2827	0.00

* The decrease in density of Ni due to working as given by Kahlbaum, 0.95%, is too large. Streb found a decrease of 0.19% and Schlett (*Ann. d. Phys.* 26, 201 (1908)), 0.26%.

P. Goerens (*Ferrum* 10, 232, Fig. 250 (1913)) has heated low carbon steel with a degree of working of 85 per cent. to various temperatures and determined the resulting increase in density. From Fig. 81 it is seen that the density at first increases slowly with the temperature of heating, then rapidly at 500° and afterward slowly again. The rapid increase at 500° is due to the fact that at this temperature about half of the canals in iron close. The total increase of density on annealing at 1000° amounts to 0.23 per cent. and agrees well with the density increase found by Kahlbaum for piano wire.

The percentage decrease of density on deformation by wire drawing is very different for different metals. While it is less than 0.01 per cent. for Cu and Sn it amounts to 0.5 per cent. for Au, Ag and Cd, and increases to 0.1 per cent. for Al and Pt and finally reaches for Fe and Ni the values of 0.25 and 0.95 per cent. This very considerable difference is due to the fact that by gliding through translation no space canals are found, while if twinning lamellæ originate in the

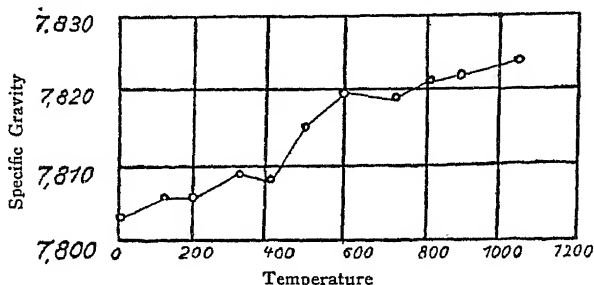


FIG. 81

gliding, space canals form. Correspondingly by the exclusive formation of translation planes in metal crystals a very small, barely detectable density lowering would be expected and by gliding through simple displacements a great decrease in density would be expected. O. Mügge (*Neues Jahrbuch f. Min.* (1899), II, p. 55) has observed only translation in the crystals of Cu, Ag and Au while in Fe simple displacements are responsible for an abnormal amount of the gliding.

If the origin of gaps by simple displacements causes the increase in volume of metals by their deformation it follows from this that appreciable volume increase can only result from a deformation involving simple displacement. For this it is necessary that a shearing force be applied to the conglomerate. The transient working of a hydrostatic pressure that develops no permanent deformation and therefore no glide planes cannot therefore cause any permanent volume increase. After the action of a pressure of 12,000 atm. applied to the metal pieces through castor oil G. Kahlbaum has observed deformations and corresponding volume increases that were very trifling compared to those observed by wire drawing. Now it can be shown (*Kristallisieren und*

Schmelzen, p. 264) that castor oil itself at 15° , the experimental temperature of Kahlbaum, is transformed into a new phase by pressures exceeding 4000 atm., and apparently the castor oil is crystallized thereby. Consequently the pressure field in a metal surrounded by castor oil is not uniform and therefore deformation took place in the first experiment of Kahlbaum and the trifling volume change resulted.

That a homogeneous hydrostatic pressure field exerts no permanent influence on the shape and volume of a metal, if the pressure amounts to 10,000 atm., is agreed by G. Kahlbaum, W. Spring and J. Johnston and Adams and we may therefore add that hydrostatic pressure also exerts no influence on the elastic limit of metals (O. Faust and Tammann, *Zeit. phys. Chem.* 75, 108 (1910)). If, however, one assumes that the volume increase of metals results from the formation of a new phase, two questions arise, which the defenders of this assumption cannot satisfactorily answer; why does a hydrostatic pressure act differently than an inhomogeneous pressure field and why in an inhomogeneous pressure field does not the phase of smaller volume form at the place of higher pressure as we would expect from thermodynamics.

Bismuth, whose abnormal volume change on melting makes an abnormal equilibrium diagram for this metal, has had an especial interest for those who wished to trace the change of properties in metals by permanent deformation to the formation of a new phase since it was hoped to find a support for the assumption of a new phase in the behavior of this metal.

W. Spring (*Bull. acad. Roy. Belg.* (3) 6, 537 (1883)) found that the density of wires of Pb, Sn, Cd, and Ag increased by annealing but that the density of a bismuth wire decreased. In this abnormal behavior of the bismuth wire Spring saw a support for his assumption that by flowing of metals a transient melting took place, after which a part of the metal remained in the amorphous state. J. Johnston and L. H. Adams (*Z. anorg. Chem.* 76, 274 (1912)) have, however, shown that the Bi data of Spring are not correct. Extruded Bi wire increases its density on annealing like other metals by about 0.8 per cent.

Johnston and Adams sought also, as did Beilby (*Phil. Mag.* (8) 6, 261 (1904)) and his predecessors, to trace the volume increase on the deformation of Bi to the formation of a new phase. They assumed that by extrusion of Bi wire a transition curve of Bi was exceeded and that hereby a new phase analogous to ice III was formed. Although such a transition curve apparently exists with Bi it is still not necessary to conclude that this transition curve is exceeded in the preparation of the Bi wire. Further Johnston and Adams have overlooked that on thermodynamic grounds the Bi phase which is stable at high pressures necessarily has smaller volume than the known crystalline Bi. Considered from the standpoint of Johnston and Adams there is to be expected not a volume decrease but a volume increase by annealing the extruded Bi wire.

At the present time we may no longer arbitrarily assume the existence of new phases. In special cases such assumptions are in conflict with the equilibrium laws in three ways: (1) assuming a phase change in fields of existence where it cannot occur, (2) reaching a conclusion which would involve opposite volume changes from the observed ones, and (3) by assuming a phase change, one is still not able to explain the difference in the action of a hydrostatic and an inhomogeneous pressure field.

19. The Change of Energy Content by Hardening.

Since in the formation of a glide surface a loosening of the molecular cohesion in the crystal takes place, work is required, and the energy content of a worked piece of metal is the greater the more glide surfaces it contains. For the work required for the formation of glide surfaces we may deduce an upper limit. If the tension on a glide surface is equal to $2\alpha_1$ and the surface content of glide planes in a unit volume of conglomerate is equal to Σg then if E is the heat equivalent of work we get $\frac{2\alpha_1 \Sigma g}{E}$ for the increase in the energy content in calories per unit volume of the material.

The increase of the energy content by the working of a metal to foil can be found if the contractile force set up in the foil by warping at high temperature is known.

One c.c. of Ag hammered to a lamella 0.19 μ thick gives a sheet of 53,000 sq. cm. surface. According to H. Schottky (p. 28) the contractile force at 300° by the warping of a silver sheet 0.19 μ thick is equal to 10 g. per 1 cm. width. The work of warping is accordingly

$$\frac{53,000 \cdot 10}{42,400} = 12.5 \text{ cal.}$$

The heat content of a silver cube of 1 cm. content amounts to 310 cal. at 300°. The energy content of 1 c.c. or 10.4 g. of Ag in the form of sheet silver is accordingly 4 per cent. greater at 300° C. than that of the compact silver.

By the gliding of a metal on its glide surfaces considerable frictional heat is developed during its deformation. The work of deformation, measured in calories, minus the calorimetrically measured amount must be equal to the glide surface energy in calories. This energy content remains in the material after the deformation as latent heat.

Such measurements have been carried out on test pieces of the purest possible Krupp iron by H. Hort. (*Mitteilungen über Forschungsarbeiten. Herausgegeben vom Verein Deutscher Ingenieure Heft 41 (1907).*) The latent energy is from 5-15 per cent. of the mechanical work. The pieces of iron were greatly elongated in a tensile machine

and the tension-elongation diagram of the bars obtained. From this diagram the work in kg. cm. can easily be deduced since the surface area between the plane of the tension elongation curve and the axis of elongation gives the work in kg. cm. (Fig. 42.) The heat evolved on elongation is measured in a calorimeter that is built around the part of the bars elongated.

That the latent energy remaining by the stretching of the bars is not to be conceived of as a transition heat into an unknown phase of iron as was done by Hort, but as glide surface energy is shown by his own findings. The latent energy is directly proportional to the hardening of the iron, as measured by the increase of elastic limit σ_1 per unit of elongation.

If by the same elongation of a bar the hardening increases greatly, the number of glide planes formed is proportional to the hardening, as microscopic investigation of other materials has shown. From the results of Hort we find that the latent heat is proportional to the number of glide surfaces in the bar. It accordingly follows from his results that the latent heat determined by him is the glide plane energy. This varies for different experiments between 0.017 and 0.091 cal. per 1 gm. iron. The heat content of 1 gm. of unworked iron at 20° amounts to about 29 cal. By stretching to the breaking point the energy content is increased 0.3 per cent.

The energy content of a worked metal is accordingly greater than that of an unworked metal and increases with the number of glide planes developed in the metal. The same action is obtained by decrease in size of the crystallites of metals.

Since with decreasing temperature the latent heat always decreases, we may assume by analogy that the same will hold for the latent heat of glide surface energy. If, however, this is the case, the specific heat of the deformed glide-surface-containing metal will be greater than that of the undeformed metal and therefore the specific heat of a metal in the finely divided state as it occurs in a eutectic will be greater than the specific heat of a metal crystal of the same mass.

However, these differences may only be very small, since if the difference in energy content of a worked and unworked metal is to disappear at absolute zero, the greatest difference to be expected for the specific heats is $\Delta E, \frac{\Delta T}{\Delta T}$. ΔE designates the difference in energy content measured in cal., ΔT the temperature interval for which the mean specific heat is determined, and T the absolute temperature of the upper limit of the temperature interval. For greatly stretched iron between 20° and 100° then we may expect a specific heat which is not more than 0.07 per cent. greater than that for iron which has not been cold worked. Since, however, the specific heat seldom is determined correctly to within 0.3 per cent., statements concerning a difference of specific heat of unworked and cold worked metals are to be accepted with caution. Recently Chappel and Levin (*Ferrum* 10,

271 (1913)) have not found differences exceeding the error of measurement. Also for the eutectic Bi-Cd in the fine and large grained condition, Levin and Schottky (*Ferrum* 10, 193 (1913)) have only found a difference not exceeding the experimental error.

20. The Change of the Electrical Conductivity by Wire Drawing.

We start from the assumption that the conductivity of a metallic crystal is a vectorial property and are supported in this by experiments on bismuth and hematite.

Matteucci (*Ann. chim. Phys.* (3) 43, 467 (1855)) found for a bismuth crystal a ratio of 1:1.16 for the conductivities in the directions parallel and vertical to the cleavage directions and Backstrom (*Oefvers K. Vetensk. Akad. Förh.* 8, 533 (1888)) found in hematite a still greater difference vertical and parallel to the γ axis.

Further it is known that in crystals which do not conduct electricity the heat conductivity depends considerably on the direction. Since for metals a close relation exists between the conductivity for heat and electricity (the Wiedemann-Franz law), it is accordingly apparent that in metallic crystals the electrical conductivity will be dependent on the direction.

If, however, the electrical conductivity depends on the direction of the crystal it is further to be expected that it will change if the metal that is made up of a conglomerate of unoriented crystals is given an orientation of the crystallites. A single orientation may be developed by very slow crystallization of a liquid metal fibre in the way described on p. 26. The conductivity of a crystal fibre prepared in this way must be different from that of an equal metal cylinder of crystallites not oriented with respect to each other.

We can, however, in a metal cylinder that consists of unoriented crystals bring the crystals into partial orientation by drawing the cylinder to wire. The orientation in wire drawing must accordingly correspond to a change in conductivity.

These changes can easily be determined since by heating the wire the original unoriented arrangement of the crystals may be restored.

If we compare the conductivity of a hard drawn wire with one that is in the soft state, we find that the conductivity on heating always increases. Since by heating the dimensions of the wire are not appreciably changed it follows that the conductivity vertical to the glide plane system of least friction is greater than in other directions, or that the conductivity in the direction vertical to the fibres of the hard wire is greater than in the direction of drawing.

The difference in resistance of hard and softened wires, divided by that of the soft, gives after multiplication by 100 the percentage increase of resistance on drawing. In Fig. 82 the relation of the size to the percentage increase in resistance is shown according to

experiments of Gewecke (*Dissertation Darmstadt* (1909)) and Addicks (*Am. Inst. Elec. Eng.*, Nov. 20, 1903). Addicks, who used wire with

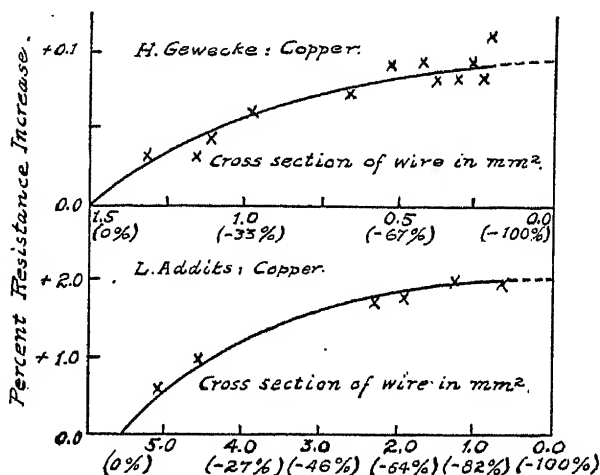


FIG. 82

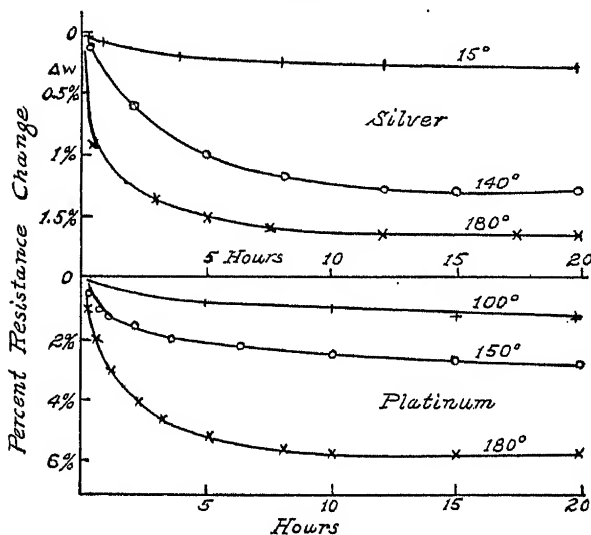


FIG. 83

large cross section, found a considerably greater increase of the resistance than Gewecke. In both cases the increase of resistance approaches a maximum value asymptotically. After the cross section

of the wire has been reduced 65 per cent. the orientation appears to be complete and the further reduction in cross section only causes the gliding of the lamellæ.

The decrease of resistance by heating of hard wires takes place in an entirely similar manner to the decrease of elastic limit on heating a deformed metal since the reversion to the original properties is determined by the same process, recrystallization. In Fig. 83 are shown the experiments of P. Cohn (*Wied. Ann.* 41, 71 (1890)) in this connection. The initial decrease in resistance is rapid and increases greatly with the temperature. At 180° a practically constant value for resistances is reached in 10 hours.

If a hard copper wire is heated for a definite time at a definite temperature we obtain, according to F. Credner (*Z. physik. Chem.* 82,

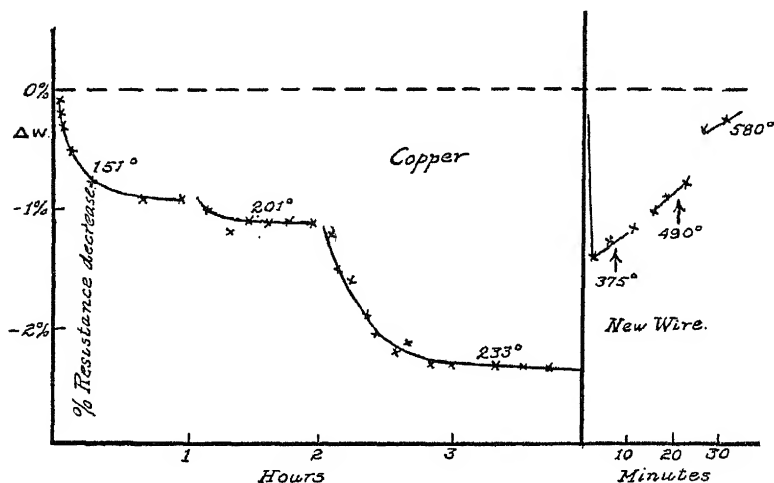


FIG. 84

457 (1913)), the changes of resistance given in Fig. 84. At low temperatures the resistance of the hard wire decreases with increasing temperature but on exceeding a certain temperature which depends on the nature of the metal, it increases. For wires of gold, silver, nickel, and iron Credner found a minimum after which the resistance increased at higher temperatures. Obviously a new process by which the resistance of the wire increases sets in at higher temperatures.

The process causing resistance decrease consists obviously of a re-orientation of the lamellæ of the hard wire. The oriented lamellæ are transformed by recrystallization into a series of unoriented crystallites, hence, the resistance decreases. Then at higher temperature, grain growth occurs and by the contractile force of the surface tension gaps form between the crystallites. As a result of this gap formation the

resistance must again increase. This gap formation can be observed microscopically. Especially at the place in which three crystallites come together gaps result on the surface of the wire. The further the grain growth continues the broader and deeper are the gaps. Fig. 85 from F. Credner shows the surface of a gold wire heated to 750° , magnified 20 times. Not only are practically all of the boundaries of the individual crystallites visible as canals but at their intersections they form depressions which obviously penetrate the wire itself.

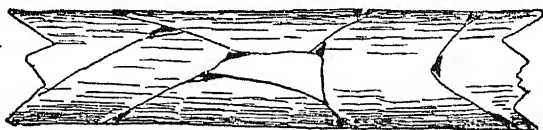


FIG. 85

If a wire will be brought to the state of minimum resistance by heating, the temperature must obviously be known where the resistance assumes a minimum value after a certain time.

If a hard copper wire is heated to successively higher temperatures for 3 minutes and its resistance in the cold state determined the resistance changes in a wire of 0.3 mm. dia. according to curve No. 1 and that of a wire of 0.4 mm. diameter according to curve 2 (Fig. 86).

For the wires investigated by Credner, he found the temperatures

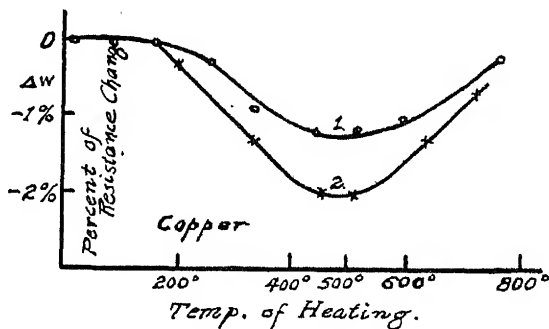


FIG. 86

of minimum resistance as given in Table 20 which also gives the total decrease of resistance in per cent. The heating time in every case was 3 min.

The conductivity of hard bismuth wire increases an unusually large amount by heating to 100° . The increase amounts to from 12-19 per cent. according to Mathiessen and Bose (*Pogg. Ann.* 155, 353 (1862)) and is apparently so great since Bi has a great difference in conductivity in different directions.

At the temperature of minimum resistance the resistance increase caused by drawing completely disappears.

TABLE 20

	Dia. of Wire	Temperature of Minimum Resistance	Total Decrease of Resistance in %	Temperature of the First Appreciable Resistance Increase
Gold	{ 0.23	480°	2.3 }	600
	{ 0.4	520	2.5 }	
Silver	{ 0.23	520	4.0 }	600
	{ 0.4	480	3.6 }	
Copper	{ 0.3	450	1.2 }	800
	{ 0.4	450	2.0 }	
Nickel	{ 0.3	700	2.8 }	Over 800
	{ 0.5	700	2.6 }	
Iron	{ 0.2	600	1.1 }	600
	{ 0.5	600	0.9 }	

If, for example, a wire is heated to the temperature of minimum resistance and the diameter decreased by drawing to about 75 per cent. and again heated to the original temperature for 3 minutes, the resistance reduced to the same cross section differs from the resistance of a wire heated to the temperature of minimum resistance shown in Table 20 by only 0.1-0.20 per cent. We can accordingly from the data given in Table 20 easily bring wires to an identical condition of structure by heating to the temperature of minimum resistance.

The increase of resistance caused by the drawing of wire through a die can accordingly be completely removed by heating to a definite temperature. This does not hold, however, for the increase of resistance which wires suffer by bending or twisting. Since by twisting or bending an orientation does not take place in the wire, but instead cracks form, it is to be expected that the increase of resistance after these deformations is permanent. We can accordingly easily separate crack formation from the action of orientation by heating the wire to the temperature of its minimum resistance, since the cracks are permanent while the action of orientation completely disappears.

Also in the temperature relation of the resistance of drawn and twisted wires an essential difference is to be expected; for torsion an influence in the temperature coefficient of resistance is not to be expected, since only cracks are developed.

On the other hand differences in the temperature coefficient of resistance for hard drawn and soft wires occur if the temperature coefficients of resistance in the various directions of the metallic crystal change in a different manner. By heating a hard wire decreases of resistance occur at 100° and even at 50°. To determine the change of resistance of hard and soft wires with the temperature these measurements must be carried on at the lowest possible temperature. If we take a hard and soft wire with the same resistance at 19.5° and

cool both to -190° in liquid air the resistance of the soft wire decreases considerably more than that of the hard. According to determinations of F. Credner the percentage difference of resistance (based on the resistance of the soft wire) between a hard and a soft wire whose resistance at 19.5° was the same, amounts, at -190° , to 8.9 for gold, 16.5 for silver, 15.6 for copper and 10.0 for nickel. From this we conclude that the resistance in the direction of the glide surfaces decreases considerably more slowly on cooling than in the direction vertical to the glide surfaces. This direction, that of the maximum conductivity, has the characteristic that for it the conductivity with falling temperature increases the greatest. Bergman (*Wied. Ann.* 36, 783 (1889)) determined the resistance of rolled metal plates to induction currents; he then heated the plates to about 300° and again made the resistance determination. The resistance decreases found by him for the plates are shown in comparison to the resistance decreases of wires in the following table:

TABLE 21

	Resistance Decrease on Heating	
	Rolled Plates	Drawn Wire
Cu	2%	3%
Al	4.5	3.5
Zn	2	2
Nickel silver	+ 0.1	- 0.2

In a rolled plate the glide planes of least friction lie parallel to the direction of rolling, hence, the induction currents which flow in these directions encounter a greater resistance than if the fluidal structure of the plates is destroyed by heating. Since rolling and drawing cause the same structure changes, they will also have the same influence on the resistance.

If a wire is placed under tension without exceeding the elastic limit, the resistance increase is very near or quite as much as by the action of a hydrostatic pressure of the same magnitude. If the tension, however, increases above the elastic limit, a permanent increase of the resistance occurs corresponding to the deformation and the change of the structure. Such permanent changes are not observed by the action of a hydrostatic pressure. Hence, resistance measurements of wires may be used to measure very high hydrostatic pressure.

Since a hydrostatic pressure does not cause a permanent change in resistance, we may not assume that the permanent resistance increases observed with rolling and wire drawing are due to the formation of a new, poorly conducting metal modification. These permanent increases of resistance are bound up with the changes of structure caused by the deformation. They have their basis in part in the fact that the resistance vertical to the bounding glide surfaces of the fibrous structure is less than in other direction and disappear by heating to the

extent to which the fibrous structure changes over to the crystallite structure.

The influence of cold working on the electrical resistance may be the summation of many factors. In the foregoing we have only considered the action of the glide directions of lamellæ that were originally differently oriented. It is, however, also possible that a part of the effect is to be traced to other causes.

According to E. Heyn (p. 91) strong tension and compressive strains exist in hard drawn wire. These have an appreciable influence on the resistance of the individual layers of the wire, but their effect in the total resistance of the wire is for the most part annulled.

Finally it is possible that by the displacement of two lamellæ along a glide plane, changes take place in the atoms themselves or their electron atmospheres by which the resistance is increased.

21. Electrolytically Precipitated Metals.

Melts of non-metallic substances upon quick cooling frequently lose the ability to go over to the anisotropic state. This can only be directly demonstrated for substances with relatively small nuclei number and not too great linear crystallization velocity. The metals occupy in this respect a separate position. By the electrolysis of solutions of their salts in water they precipitate in part as beautiful crystals (silver), and in part as crystalline masses, this crystallization resulting at a temperature frequently 1000° below the melting points. At relatively so low temperatures non-metallic substances are precipitated for the most part as amorphous masses. With metals, however, this condition of a compact mass is unknown. Even finely divided "colloidal" Au has been demonstrated by the X-ray investigations of P. Scherrer to be crystalline. (*Gött. Nach.* (1918), p. 99.) Even in particles that contain only 64 atoms, the atoms possess the same lattice as in large gold crystals. Gore, the discoverer of explosive antimony, made the assumption that it was amorphous; E. Cohen (*Z. physik. Chem.* 52, 161 (1905)), however, who has thoroughly investigated this SbCl_3 or SbBr_3 containing antimony considers it a monotropic form. Compact crystalline masses of electrolytically precipitated metals differ in their structure from that of conglomerates obtained from melts. It is very probable that the crystallites are so oriented towards the cathode that their direction of best conductivity falls in the current lines. The observations on copper show in fact, that electrolytic copper consists of crystal fibres that are club shaped on the cathode side, and the comprehensive investigations of O. Faust (*Z. anorg. Chem.* 78, 208 (1912)) and F. Credner (*Z. physik. Chem.* 82, 457 (1913)) show that the glide planes in these crystal fibres form an angle of 70 per cent. with the direction of growth.

If the glide planes were inclined 45° to the direction of growth we would expect for electrolytic copper the same elastic limit vertical or

parallel to this direction and the same elastic limit as for copper formed from the melt since in this the first gliding takes place in the crystallites whose glide planes are inclined 45° to the direction of pressure; since, however, this angle is greater with electrolytic copper, a higher value of the elastic limit is to be expected which has been confirmed by observations, and instead of 205 kg./sq. cm. for the elastic limit, 530-680 is found.

The findings of J. Bergmann (*Wied. Ann.* 36, 783 (1889)) are in agreement with this; he found that by heating an electrolytically prepared copper plate the electrical resistance decreased considerably more than with a rolled copper plate. Upon heating, the formation of unoriented crystallites takes place in both plates, and since in the electrolytically prepared plate the degree of orientation of the crystals is higher than in the rolled, and by electrolytic preparation the direction of greatest resistance for all the crystals falls in the measured resistance Bergmann found for these plates, after heating, a decrease of resistance of 4 per cent. and for the rolled plate a decrease of only 2 per cent.

Entirely similar relations concerning the elastic limit and the resistance decrease by heating are naturally to be expected also for other electrolytically prepared metals. The difference in properties of electrolytically prepared and cast copper is accordingly not due to the different natures of the two copper preparations but only to the different orientation of their crystallites.

22. The Change of the Electromotive Activity by Working.

A cold worked metal is less noble in its hard state than the same metal in the soft state. If a hard and soft piece of the same metal are placed in a solution of one of its salts, the hard piece is charged negatively since it sends more ions into the electrolyte than the soft. Since the hard piece possesses a greater energy content than the soft this difference is to be expected. The tension between two metal pieces is dependent on the condition of their surfaces. Since at temperatures where the difference between hard and soft metals is permanent a motion of the atoms in the lattice does not take place the tension depends not on the inner part of the piece but only on the surface. From this it follows that the galvanic tension difference of two pieces of metal cannot be used as a measure of the degree of work. Since the condition of the atoms not in the surface layers is without effect, a superficially hardened piece can appear less noble than a piece hardened through and through.

These conclusions are confirmed by the following experiment. The potential difference between silver wires worked in various ways and pure silver from the same piece annealed at 900° was measured at 12° by means of an electrometer. Both wires were in contact with a solution of 0.02 mol. AgNO_3 . With the soft wire against another

soft wire, potentials of less than 0.0001 volt were always observed; on the other hand, with hard wire against hard wire, differences up to 0.002 volt occurred, which decreased in three days to about 1/3 that difference. The condition of the surface of a wire after drawing may accordingly be somewhat different in different places. Hard wire against soft was in all cases negative, no matter whether it was hardened by drawing, rolling or twisting. These potential differences vary between 0.003 and 0.001 volt. The greatest difference of 0.006-0.009 volt is found by measuring emiered soft or hard wire against soft wire.

H. Davy (Wiedemann's *Lehre von der Elektricität* I, p. 723 (1893)) found that rolled Cu was negative toward soft copper. W. Spring (*Bulletin de l'Academie de Belgique*, p. 1074 (1903)) determined the potential difference between hard and soft wires and found the following.

$$t = 20^{\circ}$$

Sn	0.00011 volt
Pb	0.00012
Cd	0.00020
Ag	0.00098
Bi	—0.00385

with the exception of Bi the hard pieces are always negative toward the soft.

This exceptional position of bismuth cannot be confirmed. Further with bismuth an emiered cast electrode is negative to an unemiered and the potential difference amounts to 0.0002-0.0005 volts.

The question whether the small potential difference of hard and soft metals is due to a change in the arrangement of the atoms in the lattice or a change in atoms themselves cannot be decided on the basis of these facts; it becomes apparent however from the following described phenomena that the atoms themselves are slightly changed by the gliding on working.

23. The Influence of Glide Surfaces on the Rate of Solution.

The Neumann lines which appear not infrequently on etching a polished plane of meteoric iron, result from the twinning lamellae (caused by mechanical strain in the meteoric iron by which a simple displacement takes place) being more rapidly dissolved than the surrounding mass. Hereby a trough originates in the surface of the section which follows the intersection of the twinning lamella with the plane of the section. The straight, thick black lines (Fig. 87 in lower part) are Neumann lines. If a piece of meteoric iron which shows none or only a few Neumann lines is worked till a polished plane shows glide lines and the piece again sectioned and etched it can easily be seen that the Neumann lines coincide with the glide lines (*Z. anorg. Chem.* 60, 428 (1908), Figs. 20 and 21). After a short

heating at 800° the Neumann lines do not appear by etching (Berwerth & Tammann, *Z. anorg. Chem.* **75**, 145 (1912)). The twinning lamellae, by which the molecular arrangement was rotated, have disappeared since the molecular arrangement is identical with that of the surrounding planes. In Fig. 87 the upper part of the meteoric iron has been heated and we see that the Neumann lines reach a straight line which was heated to a certain temperature, since their corresponding twinning lamellae have disappeared. For carrying out this experiment we need only a rod of meteoric iron which has been rapidly heated in an oxy-



FIG. 87

Artificially burnt zone of meteoric iron from Mt. Joy. $\times 68$.

hydrogen flame on one end to the melting point; it is then sectioned and etched.

Since the crystallites of deformed iron contain more twinning lamellae the further the deformation is carried, it is to be expected that the rate of solution of the iron would increase with the degree of deformation.

Osmond-Werth (*Annales des Mines* (8) **8**, 5 (1885)) Heyn and Bauer (*Mitteilungen aus dem kgl. Materialprüfungsamt* (1909) 57) as well as Goerens (*Ferrum* **10**, 265 (1913)) have shown that as a matter of fact the rate of solution of iron increases greatly with the degree of work and accordingly with the number of twinning lamellae and that with the same degree of working of the iron the rate of solu-

tion decreases with the amount of carbon in the iron. Further Heyn and Bauer as well as Goerens have shown that the velocity of solution of iron with twinning lamellae greatly decreases after heating to 500°. At this temperature the changes in properties of the iron caused by working reverse very rapidly, and the decrease of the rate of solution with increasing temperature of heating the iron before determining the rate of solution agrees well with the decrease of the tensile strength (Figs. 72 and 73). The rate of solution of iron increases accordingly with the number of twinning planes developed by deformation and decreases if these disappear on heating.

For Cu, Al and Pb, E. Heyn (Martens-Heyn, *Materialienkunde*, 11, p. 303) found the rate of solution of hard wires less than that of soft.

24. The Influence of Cold Work on the Color of Cu-Ag-Au Alloys and its Influence on the Chemical Reactivity Limits of the Ag-Au and Cu-Au Alloys.

The color of soft Ag-Au alloys containing 60-75% Au is white green. By rolling they become yellower and finally a deep yellow green. This bringing out of yellow shades is also to be observed by rolling ternary Cu-Ag-Au alloys.

The greatest difference in the color of hard and soft alloys is at the following concentrations.

		Weight Per Cent.				
$\frac{\text{Ag}}{\text{Cu}}$	Mole Au	Au	Ag	Cu	Soft	Hard
$\frac{1}{2}$	0.3	52	22	26	white-red	yellow white
1.....	0.35	55	28	17	white	yellow green
2.....	0.40	58	32	10	white green	green yellow

The color of these alloys also depends to a great measure on the degree of cold work; a stretching to double length of a soft plate brings out a definite yellow shade also the reactivity limits of chemical agents on the alloys of Au with Cu and Ag change as a result of mechanical work. The limit of reactivity of a solution of yellow ammonium sulfide on a homogenized solid solution of Cu and Au in the soft state is sharp and lies between 0.245 and 0.255 mole Au, while the plates with less than 0.25 Au become entirely black in a few hours and those with more than 0.25 Au remain uncolored in a solution of $(\text{NH}_4)_2\text{S}_2$ for at least 3 years. In the hard state this reactivity limit is not so sharp as in the soft. If Cu-Au plates which in the soft state showed a reactivity limit of 0.25 mole are elongated by rolling to three times their length, the alloys with 0.255 gold will be about half as blackened by $(\text{NH}_4)_2\text{S}_2$, those with 0.260 about one quarter, while the alloy with 0.270 is darkened and loses its luster. The appearance of the plate depends on the angle from which it is observed. If it is observed vertically it appears half blackened while if it is observed at an angle it appears entirely black. The reaction

limit of a solution of $(\text{NH}_4)_2\text{S}_2$ is accordingly displaced towards higher Au contents by rolling. The nature of the alloy, of the reagent, and the degree of working have an influence on the amount of this displacement.

With increasing degree of work the reaction limit of the natural surface is very considerably exceeded. After the alloying of Ag and Au, the pellets obtained were rolled to plates of 0.5 mm. thickness and heated for 12 hours at $900^\circ\text{--}938^\circ$. Part of these plates were then rolled further by Kuhn-Augsburg and hammered to a thickness of 7.15×10^{-4} cm. and 2.4×10^{-4} cm. The resulting foils although still not as thin as gold or silver foil were somewhat porous.

Pieces of these plates and foils were then placed in a solution of 0.5 mole Na_2S in a liter and the action of the reagent observed from time to time on the foils in the hard state. With 0.23-0.55 mole Au the color of a thin layer of Ag_2S appeared in 24 hours. With increasing Au content the rate at which the layer thickened decreased.

The rolling and hammering accordingly results in an increased chemical reactivity which is still appreciable at considerably higher gold contents than correspond to the reactivity limit of soft alloys. The action of polishing the alloys is similar to the working of them to thin foils. The displacement of the reactivity limit to higher Au contents is not however so great here as with the foil.

Polishing also displaces the reactivity limit of the reagents by whose action on the natural surface the normal reactivity limit is 0.25 mole Au or more. This observation was made in the accurate determination of the reactivity limits of the Cu-Au and Ag-Au alloys. These observations are collected in the following table:

Cu-Au	Reagent	Time of Action	Reactivity Limit	
			Natural	Polished Surfaces
Weak oxidizing agents	$(\text{NH}_4)_2\text{S}_2$	80 days	0.250	0.26-0.27
	Na_2Se_2	20 days	0.250	> 0.27
		70 days	0.22	0.22
Ag-Au	Na_2Se_2	70 days	0.27	> 0.52

With different reagents the displacement of the reactivity limit by polishing is different. The displacement of the reactivity limit to higher Au content depends on whether by the action on the natural surface the normal limit of reactivity is reached or exceeded. In the first case the polishing acts to make less noble in the second case such an action is only slight or may not be present at all.

In the soft alloys the Ag atoms are protected from the action of the $(\text{NH}_4)_2\text{S}_2$ by the Au atoms. In the hard alloys for a series of the same gold content this protection does not occur. In the surface of the soft alloys the Au atoms remain in the lattice on the removal of part of the Ag atoms and thereby their protective action is lost. Since, however, we reach a visible action of the reagent these

changes of their properties must not only take place in the Au atoms along the glide planes but also in the Au atoms of the neighboring lattice planes.

25. The Influence of the Orientation on the Thermo-electric Force.

If a temperature gradient is set up in a metallically conducting crystal, so that this gradient does not fall in the direction of a symmetry axis and two points at the same temperature on the crystal connected by an isotropic liquid conductor (e.g. a mercury column) a

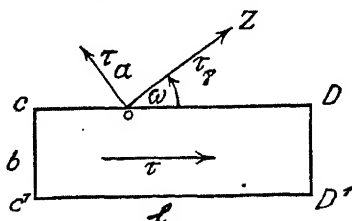


FIG. 88

thermo-electric current flows, according to W. Thomson. (*Phil. Mag.* (4) 11, 370, 433 (1856); W. Voigt, *Lehrbuch der Kristallphysik.*, p. 534 (1910); Th. Liebisch, *Grundriss der physikalischen Kristallographie*, p. 215 (1896).)

For a rod of length l and thickness b of a thermo-electrically anisotropic crystal with a symmetry axis OZ (Fig. 88) whose angle with CD is ω the following equation holds for the thermo-electric forces τ , τ_α and τ_γ .

$$\tau = (\tau_\alpha - \tau_\gamma) \frac{1}{b} \sin \omega \cos \omega$$

If the surfaces CD and $C'D'$ are held at different temperatures and the two points of the same temperature on planes CC' and DD' are connected by an isotropic conductor. For $\omega = 0^\circ$ and 90° , $\tau = 0$.

If an electric current whose intensity per unit of surface of the plane CC' is J is passed through the rod the heat absorption in the plane CD and the heat evolution in the plane $C'D'$

$$\mp \frac{JT}{E} (\tau_\alpha - \tau_\gamma) \sin \omega \cos \omega.$$

E designates the mechanical equivalent of heat and T the absolute temperature. The two amounts of heat disappear for $\omega = 0^\circ$ or 90° .

Backstrom has found the ratio, $\frac{\tau_\gamma}{\tau_\alpha}$, for hematite to be $\frac{288}{314}$ and

for rhombic bismuth Lownds found $\frac{18.4}{61.9}$ (τ_γ and τ_α in Microvolts per 1°). Accordingly not inappreciable differences of thermo-electric force are to be expected for hard and soft wire. For soft wires whose crystallites are unarranged the thermo-electric force is to be considered as the mean of the forces in the three principal directions $\frac{\tau_\alpha + \tau_\beta + \tau_\gamma}{3}$; for maximum hardened wire we must consider the force τ_g in the direction of the glide planes since in hard wire all lamellae have the same orientation.

K. Noll (*Wied. Ann.* 53, 874 (1894)) found the following thermo-forces for hard and soft wire against mercury between the temperatures of 0 and 100° . The impurities in the metals have a great influence on the thermoforce, so the wires were first investigated in the hard state and then softened by annealing.

TABLE 22

	Hard	Soft
Nickel	{ -1664	-1654
	{ -1411	-1386
Nickel silver	-1085	-1064
	{ + 4.6	- 6.0
Platinum	{ + 81.0	+ 77.0
	{ + 592	+ 594
Brass	+ 443	+ 435
	{ + 551	+ 541
Copper pure	{ + 691	+ 684
	{ + 725	+ 725
Zinc	+ 693	+ 735
Silver	+ 710.3	+ 671.5
Gold	+ 713.2	+ 713.4
Iron	+ 1601	+ 1583
Piano wire	+ 1732	+ 1729

We see that the hard wires have, as a rule, a higher thermo-force than the soft with the exception of zinc and probably platinum. The differences found by Noll merely represent the value $\tau_g -$

$\frac{\tau_\alpha + \tau_\beta + \tau_\gamma}{3}$. Pure copper is obviously thermo-electrically

isotropic but by the presence of impurities it loses this property. Also gold is thermo-electrically isotropic while silver does not appear to be. As a rule the thermoforce is greater in the direction of the glide planes of smallest friction, i.e. in the direction of greatest electrical resistance, than in the direction normal to the glide plane.

For platinum G. Borelius (*Ann. Physik.* 60, 381 (1920)) made the observation that an annealed strip in contact with a hard rolled one gave the following thermoforces: by contact with the rolled strip parallel with the direction of rolling 30.0×10^{-8} volts per degree, by contact normal to the direction of rolling 23×10^{-8} volts and normal to the rolling plane 28×10^{-8} volt.

Besides these orientation effects, the changes of properties of the atoms, such as cause the changes in chemical properties by cold working, may have an influence on the thermoforce of hard wire against soft. This potential difference disappears on recrystallization of the hard wire. The temperature of recrystallization may be determined in this way.

26. The Influence of Working on the Ferromagnetic Properties of Iron.

If an iron rod is placed in a solenoid, i.e. in a homogeneous magnetic field whose strength H may be altered and the deflections which

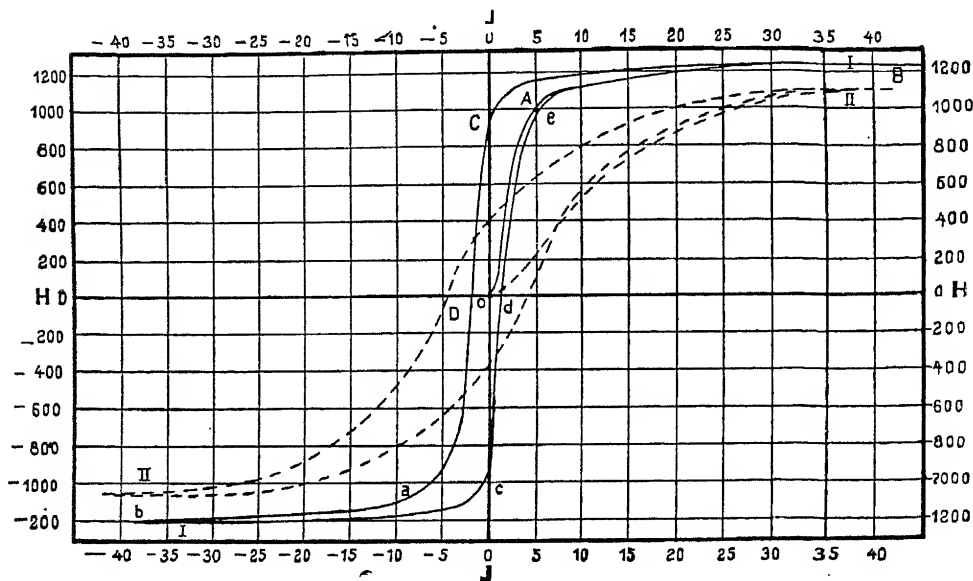


FIG. 89

the piece exerts on a compass needle measured, we may calculate the intensity of magnetization J or its magnetic induction $B = 4\pi J + H$.

In Fig. 89 the observed magnetic induction J is plotted in relation to the field strength H . If we have originally removed the remanent magnetism by demagnetizing the wire, J increases with increasing field strength H along the curve OAB to a definite saturation value. If the field strength is now decreased, J has greater values with falling field strength than occurred with increasing field strength and the J value changes according to the curve BC . The value OC of J when $H = 0$ is called the remanent magnetism. To remove the remanent magnetism of the iron rod the direction of the current in the solenoid

must be reversed. The value of J changes with increasing negative field strength along the curve CD . Then the value $-H = (OD)$ where the wire is entirely demagnetized is called the coercive force since it is the force necessary to remove the remanent magnetism.

The quotient $\frac{B}{H} = \mu$ is called the magnetic permeability of the substance while $J/H = \kappa$ is designated the magnetic susceptibility. Both properties change greatly with the field strength with ferromagnetic metals. From the course of the curve OAB it can be seen that κ has a maximum value for a certain value of H where the tangent to OAB goes through the point O .

If the magnetization of the iron rod is continued after the point D is reached, by increasing the strength of the current reversed at C , J changes with $-H$ along the curve Dab . If after saturation the field strength is allowed to decrease again to O and then the current again increased by reversing, J changes along the curve bcd , which finally coincides with the original curve OAB at higher field strengths. The remanent magnetism of the point $c(H=O)$ has practically the same value for soft iron which the remanent magnetism had at point C . Also the coercive force at point d has practically the same value as at point D .

The changes in J remain after the changes in H . This tendency is called magnetic hysteresis. Its result is that by cyclic magnetizing processes of ferromagnetic substances the magnetization curve encloses an area. This area $\oint H dJ$ the energy loss by the cyclic process in ergs; if this is divided by $42 \cdot 10^6$ we obtain the number of gram calories developed by hysteresis.

The position and form of the H - J curves and therefore also the area enclosed by them is independent of the time of a cycle. The iron bar (of 0.158 cm. diameter and 60 cm. length) considered in curve I (Fig. 89) was annealed before the experiment. The bar was then stretched about 10% of its original length and a second cyclic magnetization carried out with the worked bar. The results of this experiment are given by the dotted curve II . We see that the stretching has greatly changed the magnetic properties of the bar. The saturation value of J is lowered from 1200 to 1000. The maximum susceptibility κ is lowered from 245 at $H = 26$ to 53 at $H = 11$. Also the maximum permeability μ falls from 3080 to 670. The remanent magnetism is also lowered from 930 to 400, but the coercive force is raised from 1.7 to 4.5 and finally the energy loss by hysteresis is considerably increased.

P. Goerens has made complete investigation (*Ferrum* 10, 137 (1913)) of the changes in magnetic properties resulting from the degree of working and the carbon content of the iron. He established that the first permanent deformation by stretching the bar lowered the permeability μ more than further deformation and that this action rapidly decreased with increasing carbon content. Also the first addi-

tion of carbon lowered the permeability more than further additions. The coercive force increases nearly proportional to the degree of working and the carbon content. The same holds for energy loss by hysteresis which is determined principally by the coercive force.

The change of the magnetic properties by permanent deformation of the ferromagnetic metals is obviously to be traced to the formation of glide planes. By heating the iron the glide planes disappear (p. 82) and thereby reappear the original properties of the iron upon magnetization.

In iron, as we have seen, glide planes form by simple displacement with the resulting twinning lamellae; on the other hand the formation of translation planes is not excluded. The question is now, whether the twinning lamellae themselves or their translation planes or the otherwise present translation planes are responsible for the change in behavior on magnetization.

This we may decide from the following facts. By division of the iron rod, even if the junction surfaces are planed and polished, the magnetic induction greatly decreases, since a thin air layer remains. However, if the planes are pressed together this decrease vanishes at 100-200 atm. pressure (J. J. Thomson and Newall, *Proc. Camb. Phil. Soc.* (1887)).

From this we conclude that translation planes alone which do not so greatly loosen molecular cohesion that the electrical resistance is greatly influenced by their presence, do not influence behavior on magnetization. The action on the magnetic properties must accordingly be ascribed to the formation of twinning planes.

If we compare the action of the C-content, by which numerous needles and lamellae of iron carbide form in the iron, whose permeability is considerably less than iron, with the action of the twinning lamellae resulting from stretching, the experiments of P. Goerens show that they are similar in their action on the permeability, coercive force and energy loss from hysteresis. We may accordingly say that a twinning lamella in its action on the magnetic properties is approximately equivalent to a lamella of iron carbide. By determining the quantity of the iron in the state of twinning lamellae we may obtain our equivalence factor and establish its relation to the amount of iron carbide. If it is independent of the amount of iron carbide and also of the twinning lamellae present in the iron, the action of the two is connected by a constant. From the parallelism of the two actions we may conclude that the iron in twinning lamellae is, similarly to that in iron carbide, essentially less ferromagnetic than normal iron.

Summary

The change in properties by cold working may be explained as due for the most part to structure changes. The increase of the elastic limit by cold working is a result of the homogenizing of the internal

field of force, caused by displacements of crystallite parts along their glide planes. The density of metals in which the gliding is a simple displacement must be lowered by the formation of space canals. The energy content of a piece of metal increases by cold working. The changes of properties by cold working are in many ways similar to those produced by the additions to a metal of substances which form solid solutions. In both cases the material is strengthened and the electrical resistance increased. A certain degree of cold working and a certain addition may have the same influence on one property, but the influence may be different for different properties.

By the development of glide planes the space lattice itself does not change appreciably although small changes take place in the atoms themselves, through which the atoms become a little less noble.

The action of working on the electrical conductivity is apparently a result of the similar orientation of the lamellae, which in the direction of the glide planes of least friction possess the greatest electrical resistance. It is possible that the resistance vector is increased by the process of displacement along the glide planes. The explanation of the change of the modulus of elasticity, shearing and torsion by cold working is not apparent.

For recrystallization the principles are given that allow this for long too little considered process to be understood. Two crystals in contact are in general not in equilibrium; only if the contact takes place so that the lattice of the two crystals form a single lattice or if the contact plane is a twinning plane will no new formation of at first very small crystallites take place by sufficient increase of temperature. If these conditions are not met, new crystal formation takes place, except where the direct contact of the crystallites is prevented by the interstitial substance in which all the impurities collect with which the crystallites are saturated.

II. BINARY SYSTEMS

It is necessary that we have a knowledge of the equilibrium in heterogeneous systems to be able to understand the formation of solid alloys upon fusing two metals. We will confine ourselves to that portion of equilibrium existing between crystalline and liquid phases and the equilibrium between two crystalline varieties of different compositions. The equilibrium between vapor and liquid mixtures as well as between vapor and crystal mixtures will be omitted as they are not a part of this subject.

When any liquid mixture is cooled, the changes which take place in the mixture can be ascertained quantitatively from the equilibrium diagram for the mixture of the two metals. It not only shows what kind of crystals can exist in a series of alloys within certain concentration intervals, but also in what way and at what temperature the crystals will be formed.

This chapter will discuss the derivation of the equilibrium diagrams which can be obtained by various methods.

It is known that the derivation of the equilibrium diagram proceeds from the conception of the thermodynamic potential which is due to Gibbs (J. W. Gibbs, *Thermodynamic Studies*, Leipzig, Engelmann, (1892)) and which was adopted in the studies of Rijn van Alkemade (*Zeit. f. phys. Chem.*, 11, 289 (1893)) and B. Roozeboom (*Zeit. f. phys. Chem.* 30, 395 (1899)). The derivation of the equilibrium diagram however can be made quite elementary and will be dealt with in that manner.

The equilibrium diagrams which describe the changes of mixtures in the concentration-temperature planes occurring by changing the temperature and concentration, can also be constructed from the heat contents; volumes and other properties. These properties present a very good insight regarding the relation of the given property to the temperature and concentration of the mixture. The surfaces of heat content are of great importance in thermal analysis.

Certain conditions: complete or partial miscibility, the lack or appearance of compounds, correspond to certain idealized equilibrium diagrams.

The true equilibrium diagrams correspond either to the ideal or are formed through juxtaposition of two or more ideal diagrams. While there are no two true equilibrium diagrams, which are identical with each other, they can nevertheless be resolved into a not very large number of ideal diagrams or a series of diagrams.

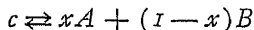
Eight typical diagrams will be discussed for the process of crystallization of liquid binary mixtures.

A. The Equilibrium Diagram

The equilibrium temperature of a crystal with its melt will be lowered at constant pressure by the addition of a foreign substance which is soluble in the melt, but not soluble in the crystal. This fact makes possible the derivation of the equilibrium diagram for a simple case.

1. The Two Substances A and B form neither Compounds nor Solid Solutions and Miscible in the Liquid State in all Proportions.

If perpendiculars to the axis of concentration AB are erected proportional in length to the temperatures of the equilibrium between the melt and crystals (Fig. 90), the curves through their upper limits will proceed from the melting points of the components A and B , the points a and b , to lower temperatures. These two curves on the temperature-concentration plane, will intersect at a point c , the eutectic point. The curve ac connects the points in which the crystal A is in equilibrium with melts of different compositions, and the curve bc likewise connects the points in which the crystal B is in equilibrium with melts of different compositions. The point of intersection c is important since the melt of the composition c is in equilibrium with crystals of A as well as crystals of B . If heat is extracted from this equilibrium mixture, consisting of melt c with the crystals A and B , A and B will separate from the melt c in such a ratio that the composition of c remains unchanged until the mass is entirely solid. Conversely if the crystallization of the melt c proceeds in this manner by heat extraction, the temperature of the mixture will not change during crystallization. Investigations have shown that the melt c crystallizes from start to finish at the same temperature, which agrees with the following reversible equation:



In this equation x represents the quantity of A , $1 - x$ represents the quantity of B , when the amount of the melt is assumed as unity. The equilibrium diagram is divided by the curves ac and bc into four fields of equilibrium. In field 1 which is above both of the curves ac and bc , all mixtures are liquid. In field 2, mixtures of A crystals with melts of different compositions exist. In field 3, mixtures of B crystals with the melts of different compositions exist and in fields $4a$ and $4b$ all mixtures are completely crystallized.

In an ideal diagram the substances A and B are of definite com-

position, consequently the state of a mixture of the composition n at the temperature t_n can be ascertained by determining in which field the point n , t_n falls.

The amount of both phases which are in equilibrium at the point n , t_n can also be determined. If the point n , t_n falls in field 3, the B

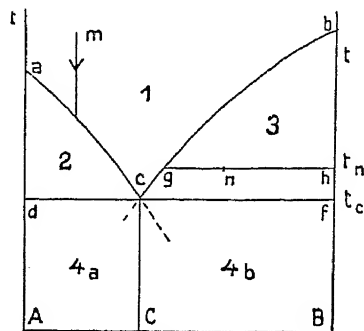


Diagram 1

FIG. 90

crystals are in equilibrium with the melt g ; the amount of crystals and melt, as one can easily determine, will vary as the distance from gn to hn . If a unit mass of the mixture n is divided into the mass x of the melt of the composition g and the mass $1-x$ of the crystals of the composition h then the equation:

$$n = xg + (1-x)h$$

must be applicable. By calculating the values for x and $1-x$:

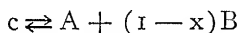
$$x = \frac{n-h}{g-h} \text{ and } 1-x = \frac{g-n}{g-h}$$

$$\text{and } \frac{x}{1-x} = \frac{n-h}{g-n} = \frac{nh}{gn}$$

$$\text{or } x \cdot gn = (1-x) \cdot nh.$$

Letting the distance gh be represented by a lever supported on a fulcrum n , and the masses x and $1-x$ attached, one to each of the ends g and h respectively, the lever will be in equilibrium. The relation derived between the masses and the compositions of the portions of the heterogeneous system and their total mass and total composition is therefore termed the lever-relation.

The reaction in a binary system is illustrated very clearly through the lever-relation. The reaction at the eutectic crystallization when expressed by the equation,



according to the lever-relation becomes,

$$\frac{x}{1 - x} = \frac{cf}{cd}.$$

Thus both equations can be geometrically stated as follows: the liquid mixture represented by the point c dissociates with heat absorption into crystals of A and B , whose amounts are proportional to the lines cf and cd respectively.

The equilibrium diagram indicates the course of crystallization as follows: the crystallization can begin in a melt of the composition m , when its temperature falls below the point of intersection of the curve ac and a line through the point m parallel to the t -axis. Whether the crystallization occurs at the temperature of this point of intersection or only at considerably lower temperature depends upon the cooling rate of the melt. If the crystallization has started by the formation of A crystals, the temperature and composition of the melt will change on the curve ac corresponding to the concentration of the melt as it moves toward B . At the point c the formation of B crystals can also occur. When the melt is undercooled in relation to the formation of B crystals, its temperature and composition will change along the dotted extension of ac , until the formation of crystallization-centers of B finally occurs. Afterwards the temperature increases to the eutectic temperature t_e and the remainder of the melt crystallizes at this temperature.

This process of crystallization corresponds to a definite structure of crystal conglomerate formed from the melt m . The large primary A -crystals which are formed as the temperature and composition of the melt move along the curve ac , become surrounded by eutectic c , which consists of very small crystallites of A and B .

The crystallized conglomerates in the field $4a$ consist of primary A -crystals surrounded by the eutectic. With melts of increasing B content, the amount of A -crystals decreases, while the amount of eutectic increases. The melt of the composition c forms a pure eutectic if crystallization takes place without undercooling. The conglomerate formed in field $4b$ is similar, only here in place of the primary A -crystals are found primary B -crystals, which are easily distinguished from the A -crystals by their form and other properties.

If the primary and eutectic crystallization takes place only after undercooling, two conglomerates of the same total composition but possessing certain differences can be obtained in the interval of concentration in which the composition c lies. If the number of crystallization-centers of A is smaller than that of B , the crystallization of B will begin first on quick cooling of a melt, which is a little richer in A than the melt c . Primary B -crystals are formed as the temperature and composition of the melt move along the extension of the curve bc , and only after the formation of A -crystals, will the re-

mainder crystallize as a eutectic. The probability of the formation of A increases however with very slow cooling, hence by sufficiently slow cooling, crystals of A and then the eutectic will form. Two melts of the same composition can accordingly yield conglomerates of different structure according to the rate of cooling. The conglomerate resulting from a slow cooling rate contains primary crystals of the material having the smaller nuclei number, while that from a quick cooling rate contains primary crystals of the material having the larger nuclei number.

2. The Two Substances Form a Compound which Melts to a Homogeneous Liquid at a Definite Temperature.

The three crystalline varieties, the two components and the compound, form no solid solutions and the melts of both components are miscible in all proportions.

If a small amount of component A or B (Fig. 91) is added to the mixture of the crystals of the compound A_mB_n and its melt, the very first small addition will not alter the equilibrium temperature of the melt and crystals A_mB_n , but subsequent additions will cause a lowering of the equilibrium temperature, which increases with increasing amounts of additions. In this respect the compounds are different from their components. If a small amount of one of the components is added to the crystals of the other which is in equilibrium with its melt, the first addition lowers the equilibrium temperature appreciably. This can be smaller or greater than that effected by subsequent additions.

Accordingly, the tangent to the equilibrium curve of a component at the point corresponding to the pure component, intersects the temperature-axis at an angle less than 90° , while the tangent to the equilibrium curve of a compound at the composition of the compound, is parallel to the concentration-axis. The equilibrium curve of the compound will, then, have a maximum and not a cusp at the composition of the compound.

These peculiarities of the equilibrium curves of the compound can be explained atomically by the fact, that in the melt of the compound, not only its own molecules but those of its components are present. The first small addition of a component does not essentially change this equilibrium in regard to the number of existing molecules, and consequently the equilibrium temperature is not influenced perceptibly. The greater the dissociation of the compound in its melt, the less the effect of the additional amounts of the one of the components on the number of the molecules of the compound present, and the flatter the equilibrium curve in the vicinity of the composition of the compound. It can be seen from the shape of the melting curve, whether the compound dissociates at its melting point slightly or to a considerable extent.

The position of the melting point of the compound has the following relation to the melting points of the components. If the melting points of the components do not differ very much, and the melting point of the compound is below the mean of the components' melting points, the tendency of the isotropic molecules of the compound to change into the anisotropic state is obviously less than the mean value of this tendency for the molecules of the components. Now experience shows that the melting points of compounds with large heats of combination lie far above the average melting points of the components and that for small heats of combination the melting point of the compound does not change essentially from the average of the melting points of their components. Thus it is seen that in general,

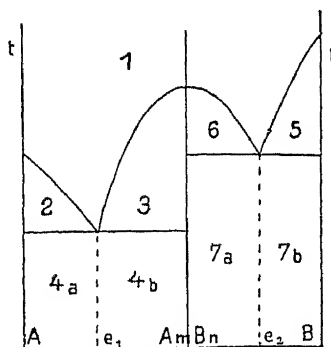


Diagram 2

FIG. 91

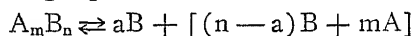
isotropic molecules become anisotropic at the higher temperatures, the lower their energy content.

The diagram for this case is illustrated in Fig. 91. The equilibrium curves of the components intersect that of the compound A_mB_n at the two eutectic points e_1 and e_2 . The number of phase fields is increased to 7. The following predictions may be made concerning the structure of the conglomerates. The quantity of eutectic consisting of A and A_mB_n , increases about the primary A -crystals with increasing content of B , until at the eutectic concentration e_1 , the conglomerate consists only of the eutectic. Then the amount of primary compound begins to increase, and that of the eutectic decreases. The conglomerate with the total composition of the compound consists exclusively of the crystals of the compound, hence on etching, a polygonal pattern like that of the pure components is developed. By further increase of the content of B , the variation in structure is repeated.

The perpendicular at A_mB_n divides Diagram 2 (Fig. 91) into two parts, each part being similar to Diagram 1 (Fig. 90).

3. The Compound Decomposes into one Kind of Crystal and a Melt.

It frequently occurs, especially when the difference of the melting points of the components is large, that the compound does not melt into a homogeneous liquid, but dissociates at a definite temperature into a melt of a definite composition and a crystalline variety of a higher melting point, which is either another compound or a component. This reaction takes place on addition of heat and reverses upon the abstraction of heat. Such a reaction will be expressed through the following equation:



a denotes the amount of B crystals in moles, and the second term the composition and amount of melt in moles, which together build a mole of the compound A_mB_n . The equation can be reproduced geometrically very easily, if the concentration-axis expresses the composition in mole per cent. 1 mole A_mB_n , point c (Fig. 92) decomposes with heat evolution at the temperature of the equilibrium into the melt $[(n-a)B + mA]$, point a , and aB crystals, point b . The

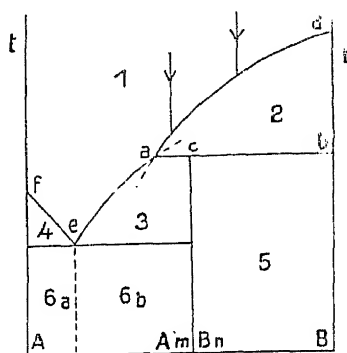


Diagram 3

FIG. 92

amount of the melt and of B crystals into which 1 mole of A_mB_n dissociates is expressed in the proportion,

$$\frac{(n-a)B + mA}{aB} = \frac{cb}{ca}.$$

The equilibrium curves of the crystal B and of crystals A_mB_n with melt $[(n-a)B + mA]$ must pass through the point a . In addition, the first must pass through the melting point of B , point d , and the second will intersect the equilibrium curve of the crystals A at the eutectic point e . The two equilibrium curves must intersect in such

a way at point a , that the extension of da falls in the phase field 3 and that of ea in the phase field 2.

The crystallization path of a melt, which is richer in B than the compound A_mB_n , will end at the point a , if the B crystals first deposited from the melt, completely combine with the melt a to form the compound A_mB_n ; if that is not the case, a remainder of the melt relatively rich in B remains, which is poorer in B than the compound. This will then, as with all melts poorer in B than the compound, precipitate the compound after the formation of it from B and the melt a has ceased, whereby the temperature and composition of the melt would move along the curve ae till the point e is reached, at which place the remainder of the eutectic will crystallize with the separation of A and A_mB_n .

The formation of the compound with heat extraction goes on at the boundary between the crystals of B and the melt a until either the melt or the B crystals are used up. When it takes place by diffusion of the B crystals into the melt, then the B crystals need not become enveloped by the crystallization of the compound if the region of grain formation is not essentially the area of the B crystals. When however the formation of the compound takes place through the diffusion of A -molecules from the melt into B crystals, then an enveloping of the B crystals must occur by the compound.

Whether the reaction in this case takes place completely or only partially will depend on whether the crystals of the compound at the temperature concerned are permeable or impermeable to the A -molecules. When the A -molecules are able to diffuse through the crystal layers of the compound, the reaction can become complete, otherwise it is impossible. It seems, however, that none of these compounds are completely impermeable to the molecules of their components, because when a conglomerate, which shows upon microscopic investigation a complete envelopment of the B crystal by the compound, is heated several hours to a temperature a little below the temperature represented by the horizontal line ab , the edge of the compound around the B crystals becomes distinctly wider. In many cases a heating period of a few hours is sufficient to completely convert the enveloped B crystals into the compound.

When the B crystals become completely enveloped by the compound the crystallization from the melt between A_mB_n and B will terminate first at the eutectic point e . Due to the enveloping of B by A_mB_n , three thermal effects instead of two are found on the cooling curve of this melt, corresponding to the separation of B , the formation of A_mB_n and the crystallization of the eutectic e . Heating such a conglomerate almost to the temperature represented by the horizontal line ab causes the amount of compound to increase, and the amounts of B and eutectic to decrease with time. These effects can be shown thermally or microscopically. By sufficient exposure of the conglomerate at this temperature the reaction is frequently completed.

4. The Two Substances in the Liquid State are not Soluble in all Proportions in one another and form neither Compounds nor Solid Solutions.

When two liquids which are not miscible in all proportions are mixed, they will form in a certain concentration interval two liquid layers. The composition of both liquid layers can be ascertained according to the method proposed by Alexejew (*Wied. Ann.* 28, 305 (1886)). A number of mixtures of known compositions are made and heated until a homogeneous mixture is formed, they are then slowly cooled and the temperature observed at which the turbidity of the mixture appears. The turbidity is produced by small drops of the second layer, which form in the homogeneous liquid upon cooling. The small drops gradually collect into one layer. The

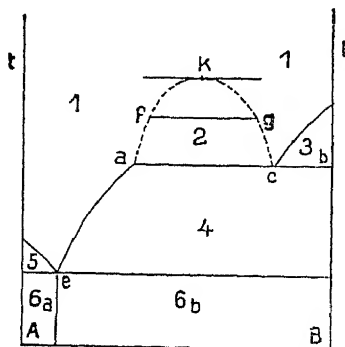


Diagram 4

FIG. 93

observed temperatures plotted on the concentration-temperature diagram will take the form of the curve $afk'gc$ (Fig. 93). Since the formation of very small amounts of the second layer produces a distinct turbidity and the turbidity as a rule appears without any perceptible supercooling, the total composition of the mixture is obviously the same as the composition of the two layers at the temperature of the turbidity. In this manner a sufficient number of points of a solubility curve can be ascertained through the determination of turbidity temperatures at known concentrations. The composition of the other layer is then easily found on the solubility curve. A parallel to the concentration axis at the given temperature intersects the solubility curve at the compositions of the two layers in the equilibrium, points f or g . According to the lever-relation the amounts of both layers, into which a mixture of any composition dissociates, are easily determined. Experience shows further that the miscibility-gap, fg , at sufficient increase of temperature diminishes with in-

creasing temperature and finally disappears at the point *k*. The two layers become identical at this point and the point *k* can accordingly be designated as the critical point. It is the maximum point of the solubility curve, and for temperatures above that of the point *k*, the two liquids are miscible with each other in all proportions.

Since the metals are opaque, the method proposed by Alexejew is not readily adaptable for determining the solubility curve of two metals partially miscible in the liquid state, and since the heat of dissociation at the formation of the two liquid layers is very small, no break occurs on the cooling curves at the temperatures of the be-

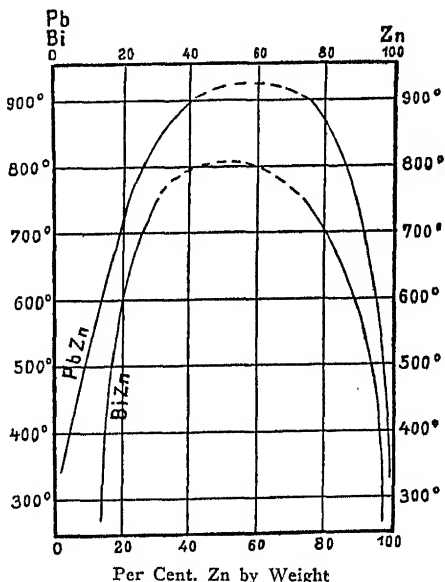


FIG. 94

ginning of dissociation. In such cases it is necessary to bring the two liquid layers into equilibrium and analyze a portion of both layers. W. Spring and Romanoff (*Zeit. f. anorg. Chem.* 13, 29 (1906)) have determined in this manner the mutual solubility of liquid lead and zinc, and of bismuth and zinc, at a series of temperatures. The two curves of Fig. 94 show these results. The composition of the layers which are in equilibrium with each other at a given temperature can be ascertained from these diagrams.

Bornemann (*Ferrum* 2, 289 (1914)) has shown that dissociation causes a very distinct break in the electrical conductivity-temperature curve. On the basis of these breaks Bornemann has determined the dissociation curve for lead and copper between 1000° and 1400°.

The equilibrium curve of the B crystals (Fig. 93) intersects the branch $k g c$ of the solubility curve. A complete equilibrium exists at the temperature of this intersection. By extraction of heat, the liquid c breaks up into B crystals and liquid a , and since the composition of the three phases is definite, this reaction must proceed to completion at constant temperature. The melts between c and b , upon cooling, first deposit crystals of B . A layer of the melt a forms at the temperature represented by the horizontal line $a c b$ during the separation of B from the melt c . Finally the melt c breaks up into the layer a and B crystals; then the B crystals separate from the liquid a , until the eutectic melt breaks up into A and B crystals at the eutectic temperature. The crystallization of the mixture of the two liquid layers between a and c begins likewise with the formation of B crystals and ends as for all melts at the eutectic point e .

We have six fields of existence to differentiate. In field 2 homogeneous liquid mixtures are not capable of existing; the mixture whose total-composition and temperature fall in field 2, consist of two liquid layers.

We may make the following predictions concerning the structure of the conglomerate obtained by the fusion of A and B . If during the crystallization a diffusion does not take place between the two layers a and c , the layer c at the completion of crystallization will consist of B crystals, between which small drops of the a -layer will be entrapped. These small drops themselves will consist of B crystals and the eutectic c . The a -layer will have the same structure as these small drops.

5. The Melt of the Compound Separates into two Layers.

The case that a compound forms by the fusion of two layers, which dissolve completely in each other only at high temperature is seldom found. At the temperature represented by the horizontal line $a b$ (Fig. 95) the compound $A_m B_n$ breaks up on heating, into two immiscible liquids a and b . On cooling, the crystals of the compound $A_m B_n$ form at the surface of contact of the layers; practically no excess of the layers a or b remain after completion of the reaction for the composition c . The course of crystallization of this excess is easily seen from Diagram 5.

Substances, which upon fusion give two liquids which do not mix at their melting points, are the hydrates, $\text{SO}_2 \cdot 7\text{H}_2\text{O}$, $\text{HBr} \cdot \text{H}_2\text{O}$ and the sodium-zinc compound NaZn_{12} .

6. The Two Substances are Miscible in all Proportions in the Isotropic and Anisotropic States.

In such cases, the crystallization occurs over a temperature interval. In general the composition of a solid solution which is in equilibrium

with a melt is different from that of the melt; and it will contain more of the component whose addition raises the equilibrium temperature, than the melt. On the basis of these principles one can derive three equilibrium diagrams for the case of complete miscibility

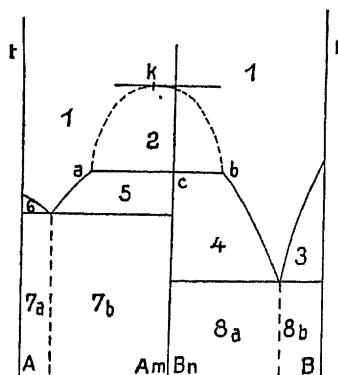


Diagram 5

FIG. 95

in the anisotropic state, which differ from each other by the form of the curves at the beginning and completion of crystallization. These curves may connect the melting points of the components without passing through a maximum or a minimum, or these curves may coincide at such singular points.

6a. A Maximum or Minimum does not Appear.

The curve of the beginning of crystallization must connect the melting points of both components for complete miscibility in the anisotropic state in such a manner that neither a discontinuity nor a break appears, and the curve of the completion of the crystallization will be lower than that of the beginning (Fig. 96). Since the two curves must meet at the melting points of the components, the distances of both curves from each other in the direction of the temperature concentration axis become greatest as a rule at equal concentration of the two components. There are three fields of existence to differentiate: Field 1, of homogeneous liquids; Field 3, of homogeneous solid solutions, and Field 2 of the heterogeneous state. A solid solution which is brought into these fields separates into a liquid and a solid solution, whose amounts are governed by the lever-relation. Thus the solid solution of the composition n will dissociate at the temperature represented by the line $a b$ into a mixture of the liquid a and of the solid solution b .

If the melt a is cooled, the solid solution b forms when the tem-

perature falls below the beginning of crystallization. Hence the melt becomes richer in *A*. A solid solution must form then from this melt which is also richer in *A* than the primary crystals. As the temperature falls, the composition of the melt and that of the solid solution will move on two different curves, that of the melt on the curve *a g* and that of the newly separated solid solution on the curve *b g*.

Two limiting cases can now be differentiated. Either no diffusion takes place between the adjacent layers of solid solutions formed, or by diffusion the composition of the primary precipitated solid solution follows the composition of the new crystals formed from the melt by the absorption of *A*.

If the latter is the case, then the crystallization will be completed when the solid solution has the composition of the original melt, in

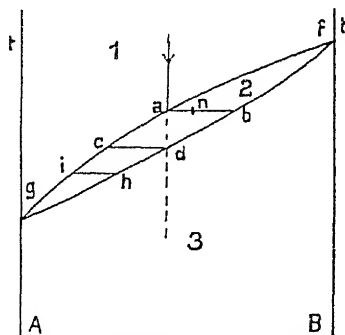


Diagram 6A

FIG. 96

other words at the temperature *d*, which is the intersection of the perpendicular for *a* on the concentration-axis with the curve for the completion of crystallization. The composition of the last remainder of the melt will be expressed by the point *c*. This kind of crystallization would correspond to the conditions of equilibrium because the entire mass of the existing solid solution has one and the same composition.

In case where no diffusion takes place, the melts, in comparison to the preceding process of crystallization, will be richer in *A* at the same temperature, and the completion of the crystallization will occur at a lower temperature. Since the last remainder of the melt *i* is richer in *A* than the remainder of the melt, *c*, the solid solution *h* formed from *i* will be richer in *A* than the primary melt *a*.

The *A*-molecules penetrate the solid solution formed more easily on slow cooling than on rapid cooling. Hence with an increasing cooling rate, the temperature interval will increase from the first limit *a d* up to a second *a h*. Consequently a change appears in the struc-

ture of the solid solution. Upon rapid cooling, layers of crystals form, whose centers are richer in the high melting substance *B* than the peripheral layers. Upon slow cooling, these differences in concentration decrease. As a rule, differences of concentration of individual layers persist even at slow cooling. This concentration difference can easily be made visible by etching the metals, since the rate of solubility of the two components is different. As a rule if a conglomerate consisting of layers of crystallites is heated to a temperature of 10 to 50° below the complete crystallization curve, then the layers of crystallites, as shown upon etching, become homogeneous throughout.

6b. and 6c. A Maximum or Minimum Appears.

If a maximum or minimum appears on the curve of the beginning of crystallization, the curve of the completion of crystallization touches that of the beginning at the point of the maximum or minimum (Figs. 97 and 98). The coincidence of the curves of the beginning and of the completion of crystallization at the maximum or minimum-point is a result of the law, that the solid solution contains more of

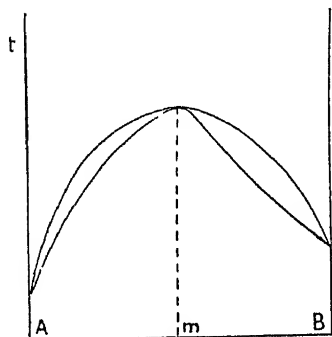


Diagram 6b

FIG. 97

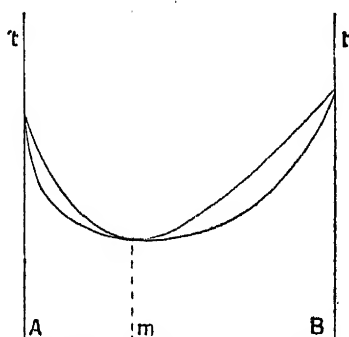


Diagram 6c

FIG. 98

the component, whose addition raises the temperature of the beginning of crystallization, than the melt.

Regarding the structure of the crystallites of which the conglomerate consists, it would be expected that in the case of a maximum in the conglomerates with more *B* than corresponds to the point *m*, the interior of the crystallites will be richer in *B* than its peripheral layers. In the case of a minimum on the curve of the beginning of the crystallization these relations are reversed.

7. Gaps in the Series of Solid Solutions.

When the two substances in the anisotropic state are not miscible in all proportions, a miscibility gap will then occur in the series of solid solutions, and we will have two different diagrams, according as the curves of the beginning of crystallization intersect below the melting points of the lower melting component or at a temperature between the melting points of both components.

7a. The Curves of the Beginning of Crystallization Intersect below the Melting Points of Both Components. (Fig. 99.)

At the temperature of these points of intersection the melt c is in equilibrium with the two saturated solid solutions d and e . By simultaneous separation of d and e in amounts which correspond to the lever-relation, the composition of the melt c remains unchanged. Therefore the melt c will crystallize completely at constant temperature without changing its composition.

The two curves, $b c$ and $a c$, of the beginning of crystallization must pass through the point c , and the two points d and e must lie

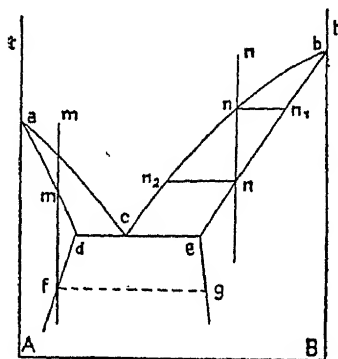


Diagram 7

FIG. 99

on the two curves $a d$ and $b c$, which indicate the completion of crystallization.

The crystallization of the melt n , whose composition does not fall in the miscibility gap $d e$, will take place as in case 6a, where the solid solution n_1 separates first from the melt n ; when these solid solutions increase upon cooling in such a manner that they are in equilibrium every moment, then at completion they will have the composition n and the remainder of the melt the composition n_2 . If the composition of the melt falls in the miscibility gap $d e$, then the eutectic crystallization occurs with simultaneous separation of d and e

after the primary separation of the saturated solid solutions e or d .

The two saturated solid solutions d and e are not only in equilibrium with the melt c but also with each other at the temperature of the eutectic crystallization. When the melt c has disappeared after the completion of crystallization, the equilibrium between the two saturated solid solutions will exist even at lower temperatures. The compositions of the existing solid solutions which are in equilibrium are determined through two points for each temperature; the line $d f$ connects the one series of these points and the line $e g$ the other. When the solubility of B in A and of A in B decreases with diminishing temperature, as that for liquids or of a liquid and a crystalline variety, the miscibility gap as a rule widens with diminishing temperatures, in which case the two lines $d f$ and $e g$ will diverge in the direction towards lower temperatures.

The widening of the miscibility gap with diminishing temperature results in a structural change in a series of solid solutions as follows, lamellae of the saturated B -rich solid solution of the composition g form in the solid solution m . If this dissociation occurs there will be six series of alloys of different structures; if it does not occur, only four series. In the first case, one has upon starting from the pure metal A , a series of conglomerates, consisting of homogeneous crystallites throughout, and as the contents increase toward B , a series of conglomerates whose crystallites are homogeneous at high temperatures but which become inhomogeneous through dissociation at lower temperatures. The third follows this series, containing a primary formed saturated solid solution d , surrounded by the eutectic; the dissociation in the anisotropic state can be observed in these constituents. The fourth series is analogous to the third, the fifth analogous to the second and the sixth analogous to the first.

Upon quenching the conglomerate, which contains only partially dissociated solid solutions, from a known temperature, it is possible to determine the temperatures at which the concerned crystallites begin to dissociate and determine approximately the coordinates of the lines $d f$ and $e g$.

7b. The Curves of the Beginning of Crystallization Intersect at a Temperature which lies between the Melting Points of both Components. (Fig. 100.)

At this temperature two saturated solid solutions are in equilibrium with the same melt and hence with each other. Upon cooling, the saturated solid solution d consists of the saturated solid solution e and the melt c , and upon heating it breaks up into the melt c and the solid solution e . Since the two solid solutions d and e are in equilibrium with each other, then a line will meet in the points d and e , and this line will indicate the composition of the saturated solid solutions at the different temperatures.

The crystallization of a melt n , whose composition falls between the points c and d , will take place in the following manner. At first, the solid solution n_1 separates, which will change into the solid solution e with diminishing temperature. This is then converted at constant temperature through the influence of the melt c into the solid solution d . Finally the solid solution n is formed from d with diminishing temperature, and n is in equilibrium with the melt n_2 at the temperature of the completion of crystallization.

Diagram 7 is closely related to Diagram 1 and Diagram 8 with Diagram 3. The assumption is made for Diagram 1, that the com-

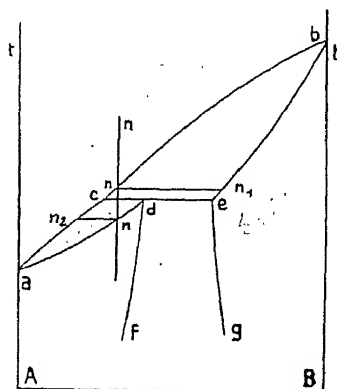


Diagram 8

FIG. 100

ponents separate from the liquid mixtures as chemically homogeneous crystals. This assumption does not hold accurately, but to such an extent that in the crystals of the one component the other cannot be detected analytically; thus colorless ice frequently crystallizes from colored water. Chemically homogeneous or almost homogeneous crystals are only seldom formed from the binary liquid mixtures of metals. However the zinc crystallizing from the Zn-Cd melts does not contain more than 0.5 per cent. cadmium and the cadmium crystallizing likewise does not contain more than 0.5 per cent. zinc (Hindricks, *Zeit. f. anorg. Chem.* 55, 415 (1907); also see Fuchs, *Zeit. f. anorg. Chem.* 109, 80 (1919)); in fact the cadmium or zinc contents of the respective crystals may be considerably lower.

B. The Surfaces of Heat Content of Binary Mixtures

The surfaces, depicting the heat content of a mixture of two substances in liquid and crystalline state in relation to the temperature

and concentration of the mixture, are made up of four kinds of surfaces; the completely liquid mixtures, the completely crystallized conglomerates and the surfaces which represent the heat content of mixtures of liquid with one or with two crystalline varieties.

The heat of mixture of two liquids as a rule may be disregarded in comparison to its heat of crystallization. The sections through the surface of heat content, perpendicular to the temperature axis, are straight lines when the heat of mixture is zero.

If the specific heat of both components in the liquid state is independent of the temperature, or its rise so slow within the temperature interval between the highest melting point and the eutectic point, that it may be disregarded, then the section perpendicular to the concentration axis through the heat surfaces of the liquid mixtures are also straight lines. The surface of heat content of liquid mixtures results, if these assumptions are correct, by gliding of a line along the isobars of heat content of liquid components; the projection of these lines on the concentration-temperature surface is always perpendicular to the temperature axis. If the specific heats of the liquid components differ, the surface formed as a result of this motion is a hyperbolic paraboloid. The sections vertical to the axis of heat content are, then, hyperbolic curves. If the specific heats are equal, these sections perpendicular to the axis of heat content become straight lines and the surface of heat content of liquid mixtures becomes a plane.

Concerning the form of the heat surface of an entirely crystallized conglomerate; E. Sommerfeldt (*Neues Jahrb. f. Miner u. Geol.* (1900), II) has found that for solid solutions the heat of mixture may as a rule be disregarded in contrast to the heat of fusion. At constant temperature the heat content will accordingly change linearly with the concentration. If the heat of mixture on the formation of solid solutions is very small, then a break will not be found on the isotherms of heat content at the concentration of the saturated solid solutions. The isotherms above the entire field of concentration of solid solution and two crystalline varieties will be a straight line, since the heat content of the crystalline conglomerate, which consists of two crystalline varieties, will always be a linear function of the composition.

Since, according to H. Kopp, the heat content of crystallizing compounds is equal to the sum of the heat contents of its components, a break will not occur on the isotherm of the heat content for the composition of the compound. The heat content of the crystallizing conglomerate will be a linear function of the concentration at constant temperatures, no matter whether appearing in the same compounds or solid solutions or only the pure components. The surface of heat content of completely crystallizing conglomerates would then result according to the former hypothesis, by motion of a line on the isobars of heat content of the components, whereby its motion will be so directed, that its projection on the temperature-concentration-plane is

always perpendicular to the temperature axis. If the isobars of the heat content of both components are straight lines, their specific heats being accordingly independent of the temperature, the surface resulting from the motion is again a hyperbolic paraboloid.

The angle at which the isobar of the heat content of a liquid component or compound is inclined to the temperature axis, is always larger than the corresponding angle formed for the crystallizing components or compound. Then the specific heat for homogeneous substances in the liquid state at the same temperature is always larger than the specific heat of the crystallized substance (*Kristallisieren u. Schmelzen*, p. 41). It is very probable that this rule applies to mixtures.

The surfaces, whose points represent the heat content of the equilibrium mixtures of a crystalline variety with the liquid, can always be considered as originating by the motion of lines. These straight lines glide on two space curves; the curve, on which the heat content of the concerned crystalline variety changes with the temperature, and the curve of the surface of heat content of liquid mixtures, namely the line connecting its intersections with the perpendiculars which are erected on the concentration-temperature-plane at the points of the curve of the equilibrium of the concerned crystals with a melt. The straight line moves in space, in the manner that its projection on the concentration-temperature plane is constantly perpendicular to the temperature axis. At constant temperature, the heat content of a mixture of a crystalline variety and the liquid with which it is in equilibrium, changes linearly with the total composition from the heat content of the crystals up to the heat content of the liquid, and since that holds for each temperature, the surface of the heat content of this mixture will be obtained in the way described. (See R. Hollmann, *Ann. der Physik.* (4), 13, 325 (1904).)

The heat content changes discontinuously at the eutectic crystallization. If the difference of heat content at the beginning of eutectic crystallization and at the end are set off in relation to the concentration, perpendicular to the x t -axis, the summation of these differences forms a triangle, whose lower side coincides with the straight isotherms of the existing conglomerate of two crystalline varieties, and whose other sides are identical with the two moving lines at the lowest temperature (Fig. 103, line $d b_1$ and $c e_1$) and also at the highest temperature (Fig. 103, line $d e$ and Fig. 108, line $c d$).

These general rules will be utilized in the construction of the heat surfaces for special cases. By the projection of the models of the surfaces of heat contents, the equilibrium diagram is found on the temperature-concentration-plane (t, x); the main points are indicated by the same letters on both corresponding figures, which will facilitate the survey of the relations of the equilibrium diagrams to the heat surfaces.

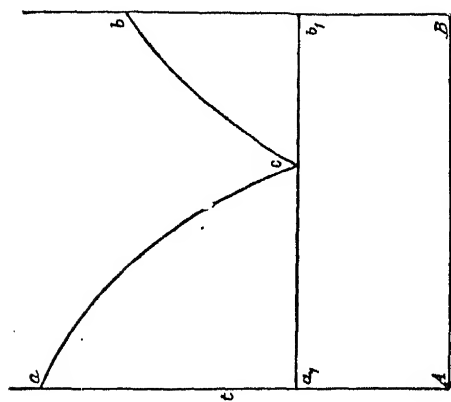


FIG. 101b

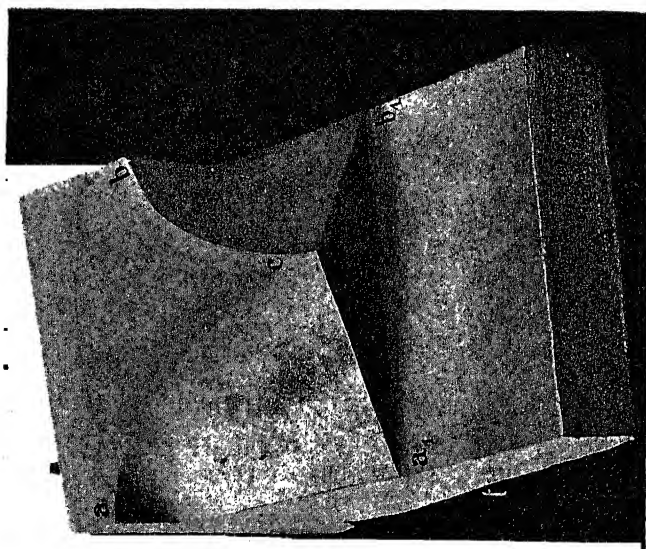


FIG. 101c

1. The surface of the heat content, for the case where the liquid components A and B are miscible in all proportions, while their crystals are not, is illustrated in Fig. 101a. The equilibrium diagram on the x, t -plane is shown in Fig. 101b. For this case the existence of both curves of the beginning of crystallization, $a c$ and $b c$, is not only characteristic, but even the discontinuous change of the heat contents at the eutectic temperature in relation to the concentration is also characteristic. The surface $a c b$ gives the heat content of the liquid mixtures, the surface $a_1 c a$ refers to the content of the mixtures of the A -crystals, and the melts with which the A -crystals

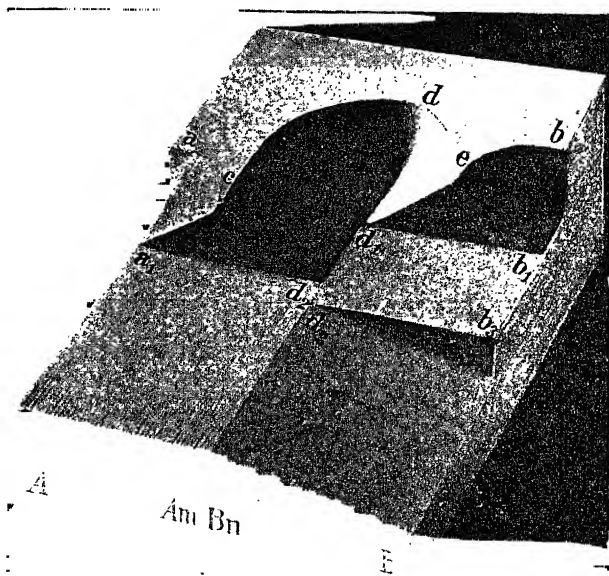


FIG. 102a

are in equilibrium at the temperature of the curve $a c$. The surface $b_1 c b$ has an analogous meaning. The plane facing forward in which the eutectic horizontal lies, indicates the heat content of the mixture of A - and B -crystals. The perpendicular distance of the lines $a_1 c$ and $b_1 c$ from line $a_1 b_1$. Fig. 101a, indicates the changes of heat content at the eutectic crystallization for a unit weight of the different mixtures.

2. When both components form a compound $A_m B_n$, which melts into a homogeneous liquid, then the surfaces of the heat contents will be shown by Fig. 102a, and the equilibrium diagram by Fig. 102b. At the melting point of the compound $A_m B_n$, the heat content changes discontinuously as for the pure components. The composition of the

compound is not only determined through the position of the maximum on the curve of the beginning of the crystallization of A_mB_n , but more sharply by the condition, that at the concentration A_mB_n , the amount of heat for the eutectic crystallization of the melts c and e becomes zero. Further the assumption is made here, that the component B has a transformation point at b_3 . At this temperature the heat content of B changes discontinuously, and this change will be found in all conglomerates which contain the crystalline variety B .

The amount of this discontinuous change of heat content will have its greatest value at the concentration B and becomes zero at the concentration A_mB_n . In the model, Fig. 102a, the heat content of

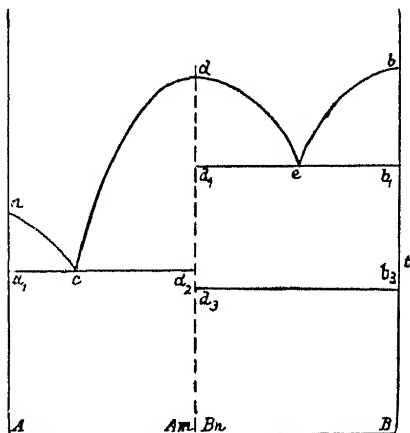


FIG. 102b

the compound A_mB_n is assumed to be somewhat greater than it would be according to Kopp's rule.

3. Seldom does it happen that the compound A_mB_n will melt into a homogeneous liquid, but rather dissociates into the crystalline variety B and a melt of the composition d . With cooling, the compound forms again at its melting temperature from B and d . The model 103a, illustrates this case. The horizontal $d e b_1$ (Fig. 103b) is the projection of the triangle $d e b_1$, which is perpendicular to the x, t -plane and perpendicular to the t -axis. The discontinuous change of the heat content, which occurs with this temperature through the reaction of B with d during the formation of A_mB_n , is expressed by the distances of both sides $d e$ and $e b_1$ of the triangle from the side $d b_1$ of the triangle, in the direction of the heat axis. The largest of these values lies at the concentration A_mB_n . The surface $d e c e_1$ results as the other surfaces of heat content of a mixture of a crystalline variety and a series of liquid mixtures, by the motion of a line, $d e (c e_1)$, which on one side rests on the space curve $c d$ and on the

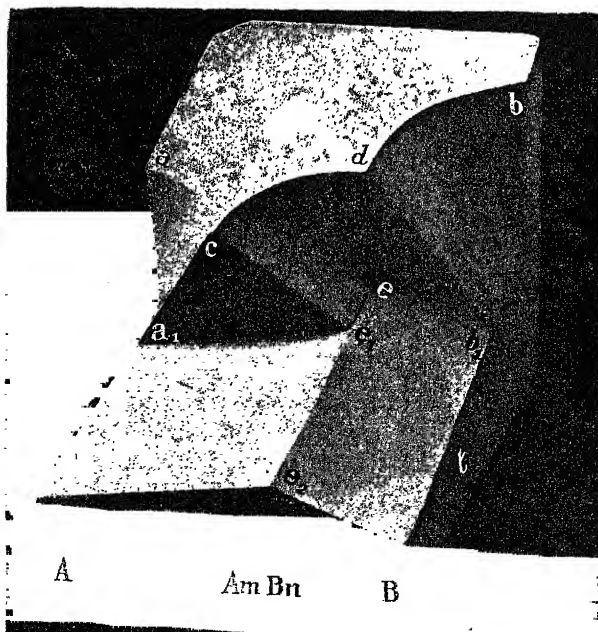


FIG. 103a

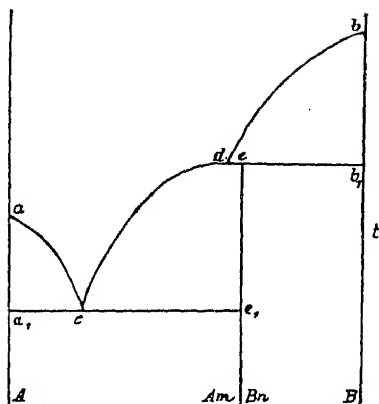


FIG. 103b

other side on the line $e e_1$. The vertex e of triangle $d e b_1$, must lie at the composition of the compound, because the one of the line $d e$ moves on the line $e e_1$ which corresponds to this composition.

In the execution of these models, the assumption is made that at

the same temperature, the heat content of the compound is greater than that computed from the heat contents of its components according to the law of mixtures. On account of this, the planes of heat content of the crystallized conglomerates which consist of A and A_mB_n and B , intersect in the line $e_1 e_2$.

4. The molten components A and B are not miscible in all proportions over a certain temperature interval, the pure components A and B crystallize from the liquid mixtures, and a crystallizing compound does not appear (Figs. 104a and 104b). When the heat of

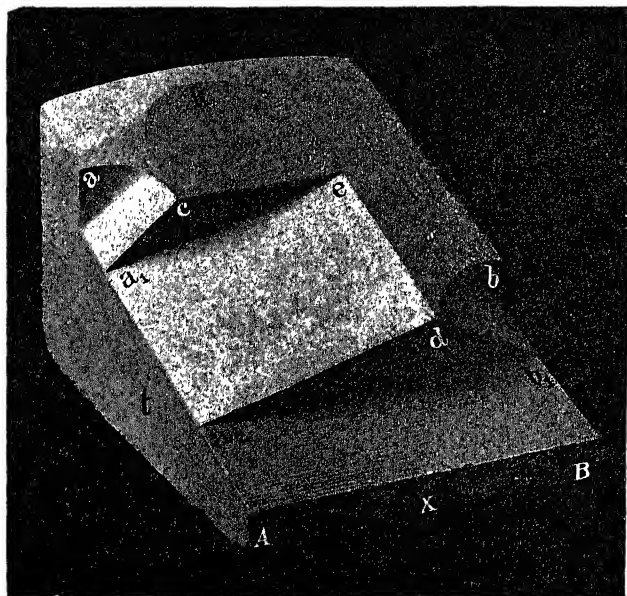


FIG. 104a

mixture of liquids A and B is zero, then the portion of the heat surface, which refers to the heterogeneous liquid mixtures, will fall in the heat surface of the homogeneous mixtures. In order to distinguish these two portions of the heat surface of the liquid mixtures, the heat of mixture in the liquid state is not disregarded. If perpendiculars are erected at the points on the curve $c k e$ (Fig. 104b), their points of intersection with the surface of heat contents produce the space curve $c k e$ (Fig. 104a). If on the so-formed space curve a line, whose end points always touch a branch of this curve, is allowed to glide, so that its projection on the x, t -plane is always perpendicular to the t -axis, a surface is formed which is limited by the curve $c k e$. This heat surface of heterogeneous mixtures is a plane, if the curve $c k e$

lies in a plane. Only in the first approximation will this be correct; however, at the scale used for representation it is difficult to distinguish the surface $c k e$ from a plane. The isotherms of the heat surfaces of homogeneous mixtures are in any case concave to the x, t -plane in the vicinity of the space curve $c k e$, for only by this form will it be able to conform to the principle of Le Chatelier. The heat content of the supercooled homogeneous mixtures at the same temperature is larger than the heat content of heterogeneous mixtures, and by breaking up on cooling, heat will be evolved.

The change of heat content at the temperature of the horizontal $a_1 c e$ (Fig. 104b) is greatest for the solution c , from which A crystallizes in the presence of two liquid layers, and becomes zero at pure A and at the concentration of the second liquid layer e . By these means,

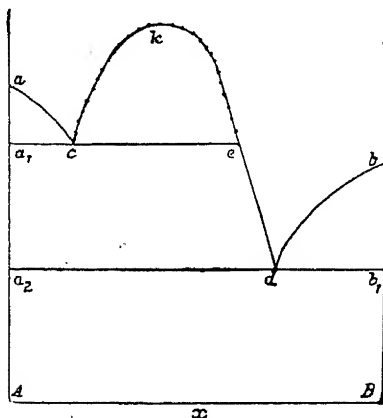


FIG. 104b

the concentrations of both liquid layers c and e , which are in equilibrium with the crystal A , are determined. The relation of the discontinuous change of heat content at the eutectic crystallization on the line $a_2 b_1$ to the concentration is the same, as in case I.

5. The crystallization of binary melts to form continuous series of solid solutions and series with gaps has been clearly discussed by H. W. Bakhuis Roozeboom (*Zeitschrift für phys. Chem.* 30, 385 (1899)). If we assume the knowledge of this rudimentary treatise, it will be possible to discuss very briefly the heat content of these systems.

The model (Fig. 105a), and the equilibrium diagram (Fig. 105b), refer to the case of crystallization of a continuous series of solid solutions for which the temperatures of the beginning of crystallization lie between those of the components. The curves of the beginning and completion of crystallization, $a c b$ and $a d b$ respectively, separate the heterogeneous equilibrium from the areas of homogeneous liquids

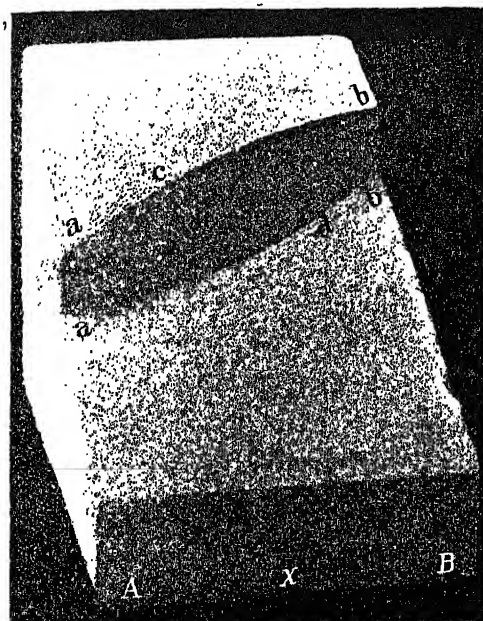


FIG. 105a

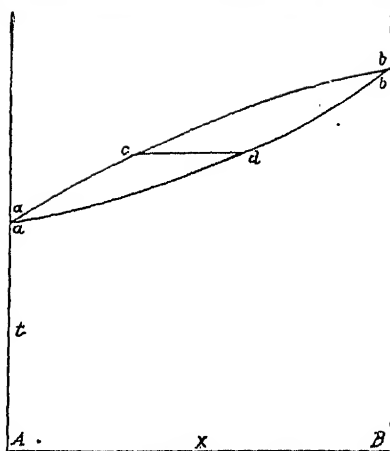


FIG. 105b

and homogeneous crystal conglomerates. The surface of heat content in this region is produced in the following manner. Perpendiculars to the x, t -plane are erected at points of the curve $a c b$ (Fig. 105b); the points of intersection of these perpendiculars with the

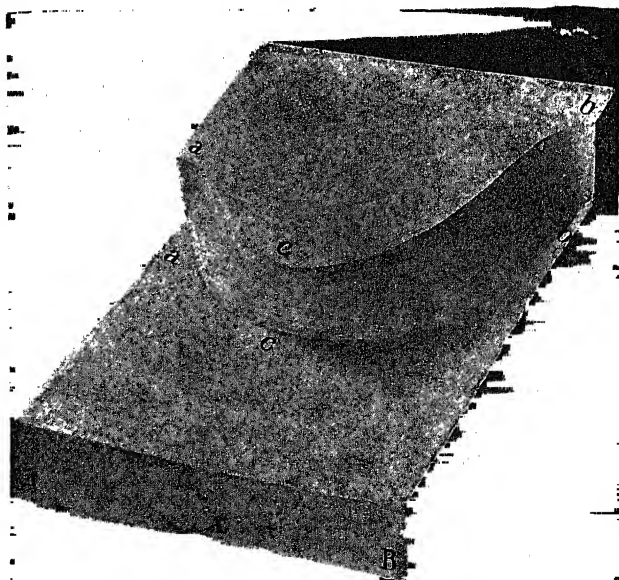


FIG. 106a

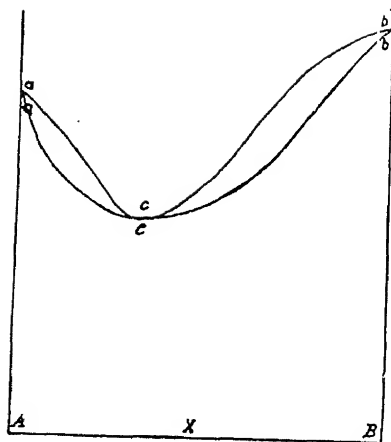


FIG. 106b

surface of heat content of the liquid mixtures, will produce the space curve $a c b$ (Fig. 105a). The space curve $a d b$ will be formed in a similar manner. If a line glides on both curves $a c b$ and $a d b$ (Fig. 105a), in the manner that during its motion, its projection on

the x, t -plane is always perpendicular to the t -axis, then the surface $a c b b d a$ will be generated (Fig. 105a).

This heat surface is entirely similar to the volume surface which was constructed earlier by R. Hollmann (*Ann. der Physik.* (4), 13, 325 (1904)). In general the surfaces of heat content give considerable information regarding the corresponding surface of volume, if the crystalline varieties form from the melt with increase in volume. The assumption that the heat of mixture is zero, and that the specific heat is independent of the temperature, corresponds to the analogous assumptions, that the volume change for the mixture is zero, and

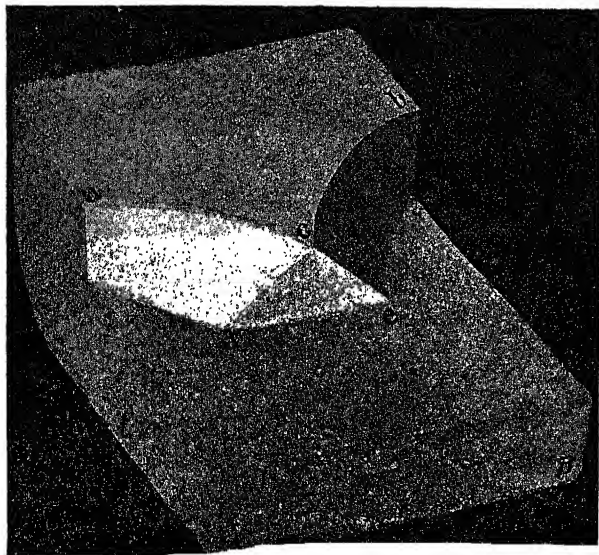


FIG. 107a

that the coefficient of expansion does not change with the temperature.

6. The heat surface for the case of a continuous series of solid solutions, in which the curve of the beginning of crystallization has a minimum, is shown in Figs. 106a and 106b. At the minimum of the curve of the beginning of crystallization, the heat content changes discontinuously as with the components. In the corresponding case, in which a maximum occurs on the curve of the beginning of crystallization, the relations are entirely analogous.

7. There are two cases to differentiate for the appearance of a miscibility gap. The curves of the beginning of crystallization slope either from the melting points of the components to a eutectic point

(Type 5, Roozeboom), or proceed in the direction of a line connecting the melting points of the components (Type 4, Roozeboom).

The relations for Type 5, Roozeboom, are shown in model, Fig. 107a, and in the equilibrium diagram, Fig. 107b. The miscibility gap at the temperature of the eutectic point c is hence determined by the fact, that the perpendicular distances from both sides $d c$ and $e c$, of the triangle to the side $d e$, become zero at the points d and e . The limits of the miscibility gap at lower temperatures are not indicated on the heat surface.

8. Figs 108a and 108b represent the heat surface and equilibrium

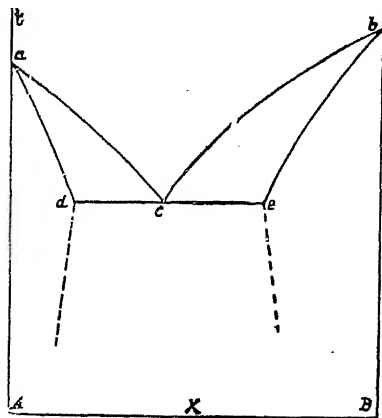


FIG. 107b

diagram for the second case. At the temperature of the horizontal $c d e$ (Fig. 108b), the solid solution forms upon cooling from the melt c and the solid solution e . The discontinuous changes, which accompany this reaction, are expressed through the distances of the line $c e$ from the two sides $c d$ and $d e$ of the triangle, parallel to the heat axis. These heat changes have their greatest value at the point d , and become zero at the points c and e . The two curves $d f$ and $e g$ are the limits of the miscibility gap, which increases with diminishing temperatures. If the heat of formation of the solid solution is not disregarded, the heat surface of the mixture of the two saturated solid solutions between the two limiting curves $d f$ and $e g$, always lies a little lower than the heat surface of the unstable homogeneous solid solutions in their region.

C. Thermal Analysis

The changes of heat content of a liquid mixture upon cooling can be derived from the surfaces of heat content. The curve sections,

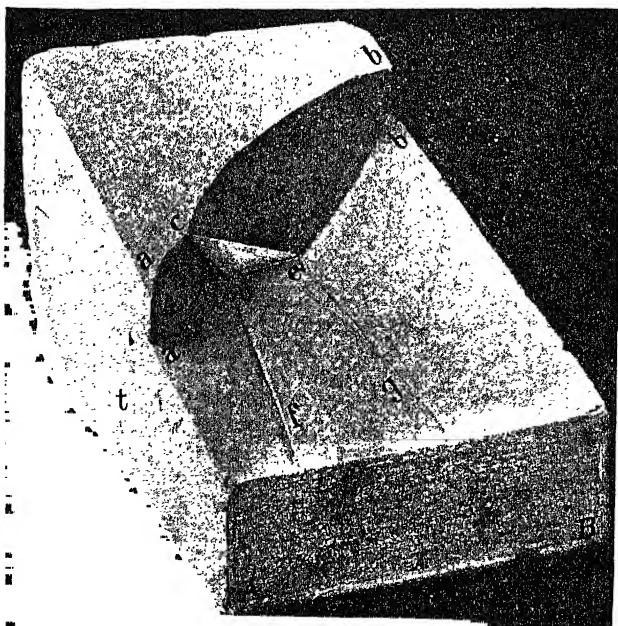


FIG. 108a

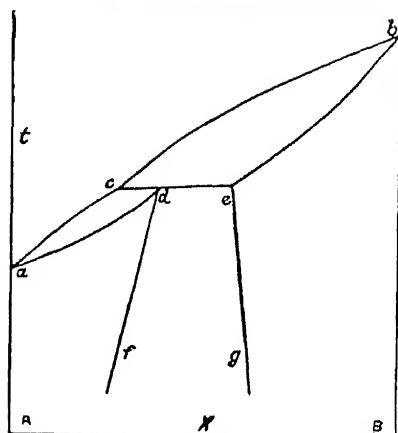


FIG. 108b

perpendicular to the concentration axis and parallel to the temperature axis through the surfaces of heat content, possesses breaks at the temperature at which the separation of a crystalline variety begins. Two kinds of discontinuities exist here; one kind, the eutectic, is

found at the temperature of the separation of two crystalline varieties, and is the same for a series of mixtures; the other is found only at a single concentration, at which the composition of a crystalline variety is the same as its melt, accordingly at the components, some compounds, and solid solutions of maximum and minimum melting points. If the temperature of a cooling melt is observed, the cooling curve, which indicates the temperature of the melt in relation to the time, will show breaks at which the temperature falls slower than at the beginning, since at the separation of a crystalline variety, heat is given out. Arrests form on the cooling curves at the temperature of discontinuities of each curve section, since the heat content decreases discontinuously at these temperatures. The duration of these arrests is proportional to the quantity of the discontinuous change of heat content, and hence changes with the composition of the melt in like manner. If the duration of the arrest is indicated graphically in relation to the concentration, it will form two sides of a triangle, whose base-line is the concentration axis. It is only necessary to observe the cooling curves for a sufficient number of melts of different compositions to gain a conception of the form of the surface of heat content and also of the surface of the corresponding equilibrium diagram. This then gives us a method for the determination of the composition of chemical compounds, saturated solid solutions, and immiscible liquid solutions, which are in equilibrium with two crystalline varieties or with a crystalline variety and another liquid solution.

One example will be sufficient to illustrate this method. In Fig. 109b the cooling curve indicates a series of liquid mixtures of the substances *A* and *B*. Inserting the temperatures of the beginning of crystallization by connecting the points of the breaks on the cooling curves, Fig. 109a, the curves *AC* and *BC* will be obtained. Further if perpendiculars, proportional to the duration of the arrests, are erected to the concentration axis, Fig. 109a, the ends of these perpendiculars will lie on the sides of the triangle above the concentration axis *cd*. If one is satisfied to determine the temperature of the beginning of the crystallization, as was the case before the introduction of thermal analysis, a break on either of curves *AC* or *BC* will be easily overlooked. Even the existence of a compound would be overlooked, if it were not of the type considered in the equilibrium diagram of Case 1 (p. 149) but rather that of Case 3 (p. 154). Such an oversight can be prevented by carefully considering not only the beginning, but especially the end of crystallization. In this case, Fig. 109, the duration of the arrest disappears only for the concentrations 0 and 100; however, the time of arrest diminishes continuously toward these two concentrations, and no other kind of arrest appears. Thus the separation of a compound from the melt is excluded. The concentration of the eutectic point *C*, which appears as the intersection of the two curves of the beginning of crystallization, will, moreover,

be governed by the position of the vertex of the triangle. sooner
conclude at the completion of the investigation, that the two placed
stances, *A* and *B*, are miscible in all proportions in the liquid, the
that they form no compounds which separate from its liquid mix, the
in crystalline form, and that the miscibility of *A* and *B* in the crys- is
line state may be practically disregarded.

Regarding the determination of the duration of arrests we may

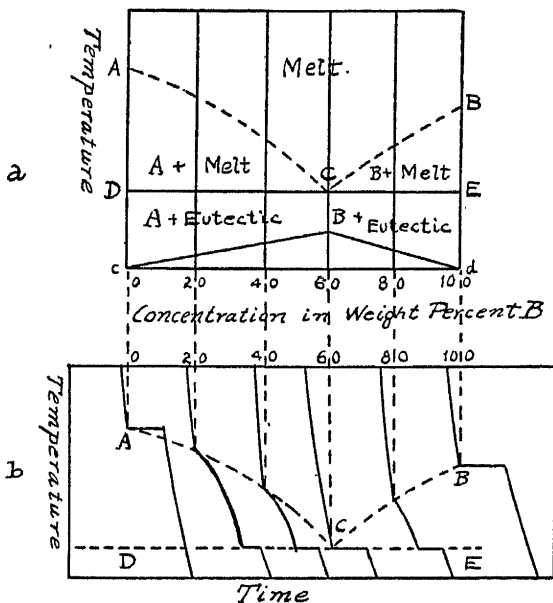


FIG. 109

state that: if the temperature of the melt at each time is known, then on a cooling curve, which gives the true temperature of the melt in relation to the time, a very distinct break will correspond to the moment of the end of crystallization. The duration, for which the temperature of the melt remains constant, will then be easily ascertained, since under similar cooling conditions of like amounts of different mixtures, the duration of crystallization is proportional to the amount which crystallizes at the temperature t_1 . Hence the amount of eutectic, which has been formed from the different melts, can be ascertained by the determination of the duration of crystallization.

In actual cooling curves a sharp break is not always found at the period of the end of crystallization, but the temperature begins to drop slowly at first at a point *f* (Fig. 110), then gradually drops faster to the point *d*, the turning point of the cooling curve, and finally falls on the curve section *d e* with diminishing speed.

basis of this phenomenon is, that a difference is established found at the temperature of the thermal apparatus by which the cool-
eties, air is drawn and the temperature of the melt, when the amount
only heat absorbed through this apparatus is not entirely covered by the
line

sc
i

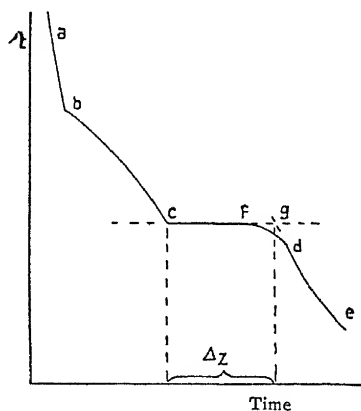


FIG. 110

inflowing amount of heat. In fact it has been observed, that if the melt is cooled in a crucible *a* (Fig. 111) with an immersed thermometer *b*, an incrustation deposits around the crucible wall as well as around the thermometer. The last portion of the melt crystallizes

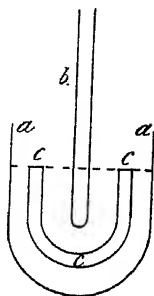


FIG. 111

in the space *c c c*, which surrounds the thermometer. The distance of this space from the thermometer depends on the relation of the heat flowing through the thermometer and crucible wall. If the flow of heat is retarded through the thermometer, by heating the upper portion of it, then the space *c c c* moves nearer to the thermometer, and the rounding off of the sharp edge *g d* (Fig. 110) diminishes likewise on the cooling curve. The more heat which flows away at the ther-

mometer and the poorer the conductance of the crucible, the sooner the temperature begins to lower and the more the point *f* is displaced towards the left on the cooling curve (Fig. 110). Nevertheless the crystallization at constant temperature proceeds with a rate, which is governed only by the flow of heat and gives for the observation of the temperature of the thermometer a slow descent towards the end of crystallization. Now the question arises, in what manner should we proceed to ascertain the duration of crystallization in a real case.

On the cooling curve there exists a well defined point, the point of inflection, *d*. Above this point the cooling curve is concave, below it, convex to the time axis. Accordingly the cooling rate increases from *f* to the point *d* and then decreases slowly from the point *d*. The increase of the cooling rate is due to the circumstance that the amount of heat, which flows to the thermometer always becomes smaller, while the amount of heat flowing away is almost constant. The subsequent decrease of the cooling rate is then caused by the temperature difference between the cooling mass and the surroundings decreasing constantly.

When no heat flows through the thermometer, the temperature will remain constant until the remainder of the melt is crystallized. This remainder then will not crystallize at a distance from, but in the immediate vicinity of the thermometer. To determine the point of time at which the last remainder of the melt crystallizes, it is only necessary to extend the curve *d e* towards *g* and find the intersection of this extension with the extension of the horizontal *c f*, the point *g*. The difference of the times of the points *g* and *c* gives then the duration of the crystallization Δz , for the case when no heat flows through the thermometer. For similar external and internal conditions of cooling and for similar amounts of melts of different compositions, the time of eutectic crystallization is proportional to the amount of eutectic. This is accordingly a method for determining the amount of eutectic.

In order to realize the same conditions of cooling, it is necessary that the crucibles be of similar shape and contain equal volumes, while the remaining conditions of cooling are to be as similar as possible. When the density of the components is similar, then similar amounts of melts will occupy similar volumes. If the densities of the components are different, it is necessary to weigh them to obtain similar volumes of melt. For similar volumes of melts, it is only necessary to divide the determined time of crystallization Δz , by the absolute weight of the melt to obtain the duration of crystallization for equal amounts of melt; these values are proportional to the amount of eutectic. Observing the temperature at intervals of 5 to 10 seconds during the determination of a cooling curve, when the amount of melt and cooling conditions are properly selected, the duration of crystallization for the eutectic melts amounts to from 100 to 200 seconds. The composition of a compound can frequently be fixed within 0.2 to 0.5 per cent. by this method.

1. The Relation between the Structure and the Thermal Phenomena in Binary Systems.

The thermal phenomena at the crystallization of liquid binary mixtures are described by the equilibrium diagram. If we can understand such a diagram, then we can deduce the thermal phenomena from the changes in concentration at crystallization. A general conception of the structure of cooled conglomerates can also be gained from the observed thermal phenomena or equilibrium diagram.

Arrests with a maximum crystallization temperature and crystallization intervals always correspond to a composition of conglomerates of crystallites, which are similar to each other. The crystallites are always homogeneous after a crystallization at an arrest of maximum temperature, but after a crystallization within a crystallization interval that need not be the case. As a rule crystallites form, whose centers are richer than the peripheral layers in the component which raises the temperature of the beginning of crystallization. Upon heating to a temperature a little below that of complete crystallization, the crystallite layers, as a rule, will become homogeneous in 1 to 2 hours. The diffusion takes place in the space lattices so that, even if hindered, it cannot be prevented.

Arrests with a minimum crystallization temperature, which lies at the points of intersection of the two curves of the beginning of crystallization, correspond on the other hand to a eutectic structure of the conglomerate. These arrests are distinguished thermally from the arrest in the minimum of a melting curve of a series of solid solutions, since these occur in the cooling curves on both sides of the crystallizing interval, the temperature of each arrest remaining the same with changes in concentration, only the duration diminishing.

If two thermal effects, a break and a subsequent arrest, occur on the cooling curve upon crystallization, the break corresponds to the formation of primary precipitated crystals, which grow on further cooling, until finally at the temperature of the arrest, the eutectic forms around them.

Thermal effects, after the termination of crystallization, can be caused by polymorphic change or by formation and dissociation of a compound. Through such reactions in the crystallized conglomerates, the structure can be considerably altered.

2. The Process of Eutectic Crystallization.

Many of the eutectics are composed of alternate lamellae of the two crystalline varieties, whence one will conceive its formation to result intermittently, in which at first the supersaturation at *A* will be broken up through the formation of the lamellae of *A*, and then the same takes place relative to *B*. The concentration at the crystallization boundary will oscillate between the saturation concentration

at *A* and *B*. By this process of crystallization, one will observe in the eutectic, parallel or concentric lamellae between alternating layers of *A* and *B*, on the other hand R. Vogel (*Zeit. f. anorg. Chem.* 76, 425 (1912)) states that the eutectic does not consist of lamellae but rather of little rods. These little rods stand perpendicular to the cooling surface, the eutectic constituent crystallizing simultaneously and not intermittently.

If an eutectic alloy of zinc and cadmium, which contains 18 per cent. zinc and 82 per cent. cadmium, is made by melting in a small iron crucible, after which the bottom of the crucible is brought in contact with cold water, then according to R. Vogel, a section perpendicular to the cooled surface gives the structure in Fig. 112 and a section parallel to the cooled surface a structure as in Fig. 113. The eutectic accordingly consists of small rods of cadmium surrounded by little rods of zinc. By the cooling, many crystallization centers of cadmium are formed on the bottom of the crucible, which grow as crystal grains in the

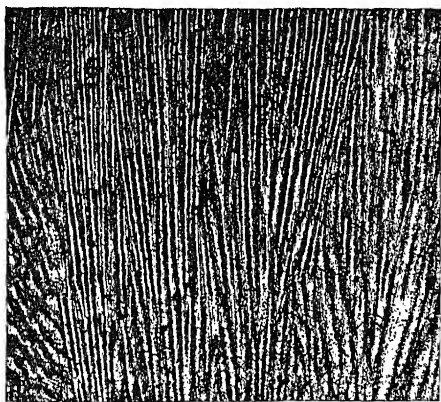


FIG. 112

Eutectic of Zn-Cd rapidly crystallized. Section perpendicular to cooling surface. $\times 68$.

melt. Obviously in this case of crystallization, the cadmium is the principal constituent since its crystal grains reach further into the melt than those of the zinc. The bright grains of cadmium are surrounded by the darker etched grains of zinc.

Upon slower cooling, crystallization centers of the one component form within the eutectic melt, which grow to spherulitic form, the other component crystallizing between the needles. Fig. 114 illustrates such a case. One can easily recognize the bright cadmium needles which radiate from about six points and by further growth come together to form boundaries. The sections through these boundaries are clearly recognized in Fig. 114, as are also the different directions

of the zinc and cadmium rods in the fields bounded by these sections.

If we cut through such a spherulitic form (Fig. 115), which is composed of relatively few black rods, at a point other than the center

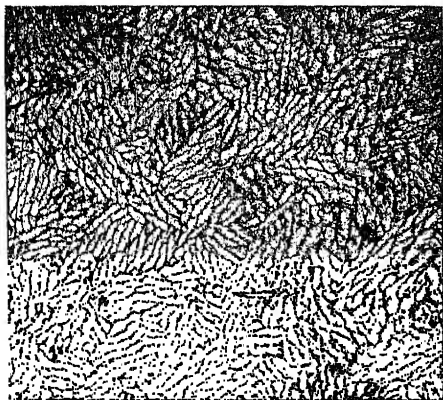


FIG. 113

Eutectic of Zn-Cd rapidly crystallized.
Section parallel to cooling surface.
× 68.

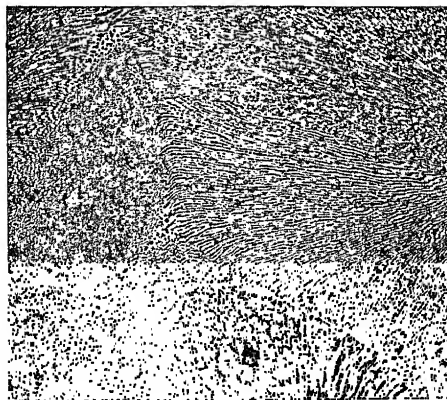


FIG. 114

Eutectic of Zn-Cd slowly crystallized.
× 68.

line, a section similar to Fig. 116 is obtained. As the section approaches the center, the peripheral portions appear as lamellae, although the spherulite is composed only of little rods. We can therefore con-

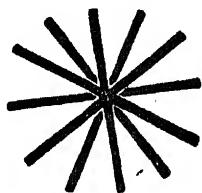


FIG. 115

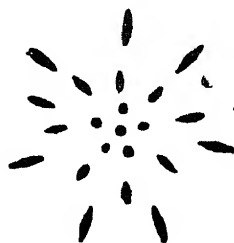


FIG. 116

sider, that at normal eutectic crystallization, the eutectic originates as spherulites composed of little crystal rods of both components. Since the crystallization of the little rods of one of the components is more rapid, it follows that the little rods of the more rapid crystalline variety will become surrounded by the little rods or cylinders of the other crystalline variety. We can readily recognize in the completed eutectic which of the two constituents plays the leading rôle.

3. Crystallization Anomalies in the Formation of Solid Solution.

A dendritic structure is frequently found in rapidly crystallized metallic solid solutions. In the crystallization of the melt, branching

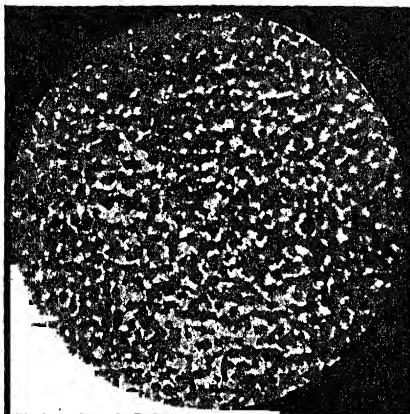


FIG. 117
Nickel steel. 25% Ni. $\times 30$.

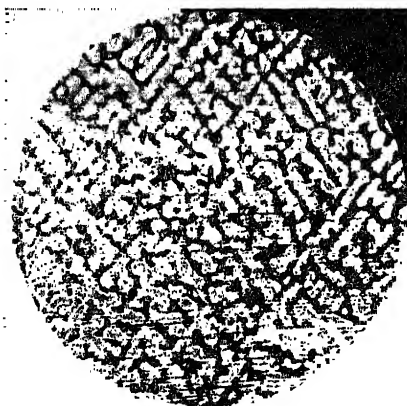


FIG. 118
70% iron + 30% manganese. $\times 40$.

needles quickly shoot out from the cooling surface and the remainder is then crystallized between the needles. The concentration difference between the needles and the ground mass formed later is considerable.

Fig. 117 shows the structure of a quickly crystallized nickel steel containing 25 per cent. Ni and Fig. 118 shows that of a manganese steel with 30 per cent. Mn. Both were etched with alcoholic picric acid solution. In the nickel steel, a low-nickel dendritic network has first formed and in its meshes, a high-nickel ground mass has crystallized. The crystallization of the manganese steel has taken place in the same way. Fig. 119 shows high-manganese dendrites formed by rapid crystallization in a Mn-Cu ground mass of low manganese content. Fig. 120 shows the effect of heating for five hours at 1050° . By still further heating the dendritic structure disappears entirely.

By long heating at the highest possible temperature, the alloys of

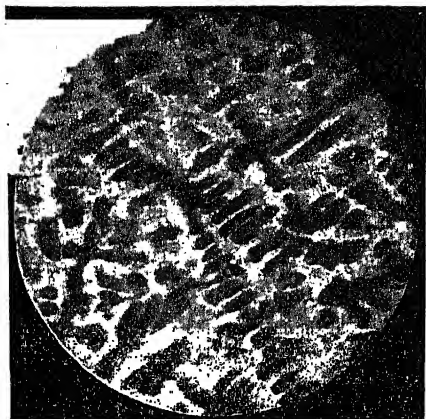


FIG. 119

30% Cu + 70% Mn. Cooled rapidly.
Etched with H_2SO_4 . $\times 68$.

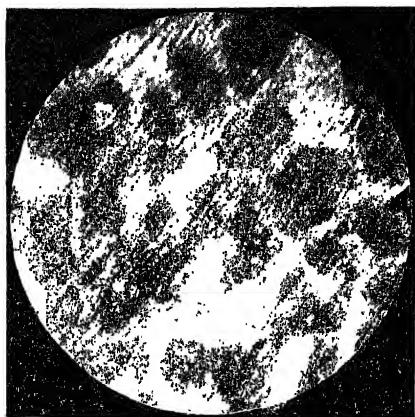


FIG. 120

30% Cu + 70% Mn. Annealed, etched
with H_2SO_4 . $\times 68$.

dendritic structure become homogeneous and their structure becomes one of polyhedral grains.

The solid solutions, which separate from the melt on rapid crystallization, do not have a composition corresponding to the equilibrium diagram, but those solid solutions form whose linear crystallization velocity is the greatest under the conditions existing. The remainder crystallizes in the network so formed.

By casting melts, which give solid solutions on crystallizing, into iron molds, that is, under conditions of rapid cooling, concentration differences occur between the outside and center portions of the alloy, which would not be expected from the equilibrium diagram. O. Bauer and Arndt (*Mitteilungen aus dem Materialprüfungsamt* (1921), p. 71) found the following compositions in the outside and center.

	Center	Outside
Cu Sn	92.7	91.7% Cu
Cu Mn	{ 26.8	28.4% Cu
	{ 84.2	83.8% Cu
Al Zn	16.1	17.8% Zn
Al Cu	2.8	3.5% Cu
Ag Cu	90.6	88.2% Ag

No appreciable difference occurs in the composition between the outside and center of quickly cooled brass with 70-75 per cent. Cu, of Cu-Ni with 77 per cent. Cu or of Hg-Pb with 77 per cent. Pb.

It would be expected from the equilibrium diagram, that the outside layer would be higher in the component, whose addition raises the temperature of the liquidus. The experiments given in the above table do not bear this out. The equilibrium diagram only describes the processes which take place with very slow cooling, and are accordingly only slightly removed from equilibrium conditions. It can in general give no information concerning the processes on rapid crystallization. The differences found are to be traced principally to the fact, that the first dendrites of solid solution to form, have the greatest possible value of the linear crystallization velocity; further, the melt flows through the dendritic network, and in this way becomes impoverished in the component, which raises the temperature of the liquidus.

4. The Microscopic Investigation of Alloys.

The nature of the formation of the alloys upon cooling of their melts is closely connected with their microscopic structure. One can readily obtain a general outline of the structure from the cooling curves, especially of the changes on exceeding certain concentrations; limits of concentration of the miscibility gaps and concentrations corresponding to compounds. The results of thermal and microscopic investigations must always agree. If this is not the case then some reactions in the crystallization of the alloys have been overlooked. The structure formed on crystallization will be more or less changed by these reactions if they entail a change in composition of the existing crystalline varieties. By rapid cooling from temperatures above that of the given reaction, the reaction can be frequently inhibited and the conglomerate obtained in a state corresponding to its formation from the melt.

The close connection of the microscopic structure with the thermal history of the conglomerate offers a convenient means for the control of thermal history and increases the importance of the microscopic investigation considerably. These investigations are made by the study of the metallic bodies with reflected light. This has two advantages over the method of photographic examination of a thin section. For the investigation by reflected light it is only necessary to prepare a smooth surface, as metallic bodies reflect light so well that very

clear images of all constituents lying in the plane are obtained. The clearness of the constituents of the small grains surpasses the images obtained in thin sections. The image in the thin section is indistinct as the constituents overlap. Consequently the structure of a eutectic is as a rule very hard to recognize in a thin section, while in the metallic bodies of the same grain size it stands out more distinctly since it is entirely in one plane.

There are three methods for microscopic investigations: 1, the investigation of polished surfaces which have been appropriately etched; 2, the investigation of polished surfaces following their subjection to pressure beyond the elastic limit; 3, the investigation of the light reflected from the polished surfaces.

The first method is the one generally used. After the specimen has been filed, the surface is further polished with the use of abrasives and finally with a rotating cloth covered disc. When the constituents are noticeably different in hardness, the hard crystallites will stand out in relief and the structure is visible without further treatment, but frequently it does not have the desired distinctness. By appropriate etching it can be made more distinct. The distinctness developed will depend on the solubility of the different substances of the various constituents in the etching solution. The best etching medium can only be found by test. To do this, small drops of the solutions are placed on the polished surfaces and their action observed. By using a medium giving a rapid etch, there is danger of over etching and thus destroying the distinctness of the image. As a rule a long experience with the use of etching mediums is advantageous and observation in the microscope will establish the time required for distinct development of the constituent. Electrolytic etching and heat tinting of the polished surfaces, producing colorations, will often give satisfactory results. The electrolytic etch, especially when the specimen is the anode in a salt solution using a current strength of 0.01 to 0.001 ampere for 1 to 10 minutes depending on the individual case, will attack the constituents equally throughout.

The second method, that of the mechanical treatment of the polished surfaces of the specimen, is naturally not applicable to brittle material. With material which will bear up under permanent deformation, this treatment for the polished surfaces is recommended since the structure appears very distinct from the formation of slip lines in the crystallites (Figs. 34 and 35, pp. 68 and 69). When there is doubt as to whether the structure of the etched portion corresponds to that of the inner structure, then the mechanical treatment of the polished surface will usually give the desired information.

The third method, the analysis of the light reflected from the constituents, depends upon the fact that optically isotropic, i.e. regular crystallites, will not resolve a light ray by perpendicular reflection while anisotropic crystallites will resolve it into two components of different amplitudes and phases. In perpendicular reflection from

crystals of the tetragonal, rhombic and hexagonal systems, these components oscillate perpendicular to one another; with the perpendicular reflection of crystals of the monoclinic or triclinic systems the light is not perpendicularly but elliptically polarized. The difference of intensity for the two rays can be made visible by a nicol, two quartz plates, or a Savart duplex plate. By this arrangement, interference bands will form. These bands do not appear by the reflection from isometric platinum and iron but do for the hexagonal-rhombic crystals of zinc, antimony and bismuth, with the exception of certain orientations of the crystals.

On this basis, Koenigsberger (*Zentralbl. f. Mineralogie* (1908), 565, 597, 729; (1909), 245; (1910), 712; also Endell u. Hanemann, *Zeit. f. anorg. Chem.* 83, 267 (1913)) constructed an apparatus which made possible the determination of the optical orientation of crystallites in metallic conglomerates. This method requires a very highly polished surface. Since the presence of polishing scratches will cause the light not to be reflected perpendicularly, the interference bands will appear upon reflection of poorly polished planes even when they consist of optically isotropic material.

Fortunately the demands which are placed on the optics of the metallographic microscopes are as a rule not very great, since the structure of most eutectic can be resolved easily at a magnification of 100 diameters. As a rule in such investigations, one can easily manage very well with a magnification up to 300 diameters.

5. Thermal Investigations of Alloys.

Regarding the practical execution of thermal investigations, the reader is referred to the practical part of the Elements of Metallography by R. Ruer (*Metallographie in elementarer Darstellung*, Leipzig, L. Voss (English translation by C. H. Mathewson; J. Wiley & Sons, New York) and the chapter "Metallographie" by P. Goerens and R. Ruer in the handbook on *Arbeitsmethoden in der anorganischen Chemie* by A. Stahler, Vol. III, p. 294 (1913)).

The behavior of substances at high temperatures until recently was little known, because with the use of gas, a temperature of only about 1200 degrees could be attained and an accurate temperature determination could only be made with difficulty.

With the introduction of the thermo-elements, especially the platinum-platinum rhodium elements by Le Chatelier, C. Barus, Holborn and Wien, a reliable instrument was produced for determining high temperatures, and sensitive for very small variations. This made it possible to use very small amounts of a substance for the determination of the cooling curve.

On the other hand, by the development of electrical technique, the old method of heating by gas was replaced and by using small amounts of substances a temperature up to 2000° could be reached with a small current.

From these conditions, the modern experimental technique for ascertaining cooling curves and the preparation of equilibrium diagrams with special consideration at the completion of the crystallization was developed in the institute at Göttingen.

For metals which can easily be handled, an amount of 20 grams is sufficient for the determination of the cooling curve. The metal is melted in a tube into which is introduced the thermo-elements protected by a tube. When the metal reacts but slightly with the protecting tube and the container, the thermo-elements can be used as a stirrer to produce a homogeneous melt. When the reaction is pronounced then it is necessary to use a rod of some inert material for stirring and introducing the thermo-elements but for short intervals during the cooling.

The thermo-elements are prepared by welding one end of a pure platinum wire to the end of platinum-rhodium wire in an oxyhydrogen flame. For a melt of 20 grams the diameter of the wire does not need to be greater than 0.2 mm. Each element is protected by a thin walled porcelain tube, which if used for stirring should be double-holed porcelain. The thermo-elements should also be protected for a distance of 2 to 3 mm. from the end of the tube.

The material for the protecting tube and melting tube are made from various materials, such as porcelain, Marquardt's mass, magnesite and fused quartz. Melting tubes of carbon and graphite frequently give excellent service. It is necessary that during the melting, the action of the melt on the protecting tube and melting tube be exceedingly small in order to limit the amount of foreign material introduced.

Fluid silicon, chromium and manganese react with porcelain considerably and eat away the thin walled porcelain tube in a short time. Silicon-rich melts scarcely affect fused quartz.

A furnace recommended for raising the temperature quickly is a carbon tube about 13 cm. long, 2 cm. inside and 3 cm. outside diameters, whose ends pass through a hollow copper backing which is water cooled. These copper backings are connected with the conductors. The carbon tube is surrounded by a layer of fine carbon, which is necessary between the carbon tube and the surrounding clay cylinder to lessen the burning-up of the glowing carbon tube. Such a carbon tube can be used for about 60 heatings when not heated above 1600°.

An alternating current of from 8 to 12 volts and 500 amperes is sufficient for the heating of such a carbon tube up to 2000°.

D. Reactions in the Solid State

The thermal investigation of mixtures of two substances has shown a series of reactions of considerable rapidity in crystallized conglomerates. These reactions take place with linear rate of transformation whose maximum magnitude is unknown, but whose amount

up to the maximum value depends only on the flow of heat, since these reactions are denoted on the cooling curve by arrests.

These reactions may be divided into three groups as follows:

1. A dissociation can appear in a continuous series of solid solutions analogous to the dissociation of a solution of phenol in water with decreasing temperature. To this class belongs the dissociation at high temperatures of saturated solid solutions into a series of solid solutions with a miscibility gap. The general reason for this reaction is a change in solubility of the two substances in the anisotropic state with a change of temperature.

2. Complete or partial dissociation in the series of solid solutions may be produced by a polymorphic transformation of a component or of a compound.

3. Two new crystalline varieties can form from the one existing or a new one can form from two different crystalline varieties as a result of the dissociation of the molecules of a compound forming.

The structure which has been formed by the crystallization of the melt will change as a result of these reactions if the concentration changes in the crystalline varieties taking part in these reactions are considerable. An abnormal case, in which the structure does not correspond to the process of crystallization, is due to a reaction in the solid state which may be noticed by more or less definite arrests and retardations on the cooling curve.

The concentrations at the maximum of these thermal effects, as well as those at which they disappear, are of fundamental importance in deducing the equation of the reaction involved. These conclusions can be confirmed by microscopic investigations.

These reactions can frequently be inhibited by quickly cooling the conglomerates from a temperature above that at which the reaction begins. The conglomerate then has the structure corresponding to the thermal phenomena. The structural changes due to reactions in the solid frequently begin when the conglomerate is heated to temperatures far below the equilibrium temperature of the crystalline varieties present. By holding the conglomerate a long time below the equilibrium temperature, the reactions in general can proceed to completion; if they do not proceed to completion, it is due to the enveloping of one crystalline variety by another.

The reactions of the first two groups are dealt with from the standpoint of the equilibrium theory by Roozeboom (*Zeitschr. f. phys. Chem.* 30, 413. (1899)) in his classical work.

I Dissociation in the Anisotropic State Analogous to the Dissociation of Liquid Solutions.

Upon cooling the solid solutions in the region of the curve *ckd*, Fig. 121, each homogeneous crystallite dissociates into a mixture of two solid solutions, whose composition is determined at a definite

temperature by the point of intersection of the curve ckd with a parallel to the concentration axis at the given temperature and whose amount is controlled by the lever-relation.

The heat of mixture of two liquid solutions, whose compositions differ a little in the vicinity of the point k , is obviously very small and disappears at the maximum point k , since both liquid layers become identical. This must be true for the heat of mixture of two solid solutions in the vicinity of the point k . Consequently the thermal effect at the beginning of dissociation can only be exceedingly small. It will increase, however, with progressing dissociation and may be perceptible on the curve ef . The temperatures of this curve do not refer to that of the beginning of the dissociation, the equilibrium curve ckd . The existence of thermal effects alone at the temperatures of the curve ef does not show that it is a question of such a dissociation; it could also be due to the formation of a compound. The structure

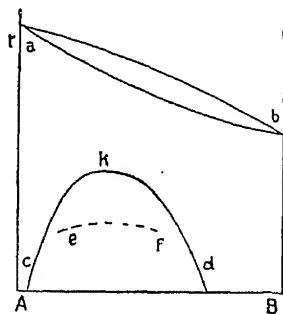


FIG. 121

of the conglomerate in which the dissociation occurs will determine which is the case.

This kind of dissociation is not found with metallic solid solutions, but is found however in the solid solutions of KCl with NaCl. (Kurnakow u. Zemčuzžny, *Zeitschr. f. anorg. Chem.* **52**, 186 (1907).)

These solid solutions become turbid between 300° and 400° after an evolution of heat has occurred in them, while KCl and NaCl do not show this appearance.

When the miscibility gap increases with diminishing temperature in a series of solid solutions, the solubility lines which indicate the composition of the saturated solid solutions in relation to the temperature, diverge at diminishing temperatures; thus the saturated solid solutions dissociate with diminishing temperatures. Crystal fibres of the component with which they are in equilibrium form in the grains of the solid solutions. Since the amount of this precipitated material is small as is likewise the heat of dissociation, retardations will seldom be found on the cooling curve. The only means for the detection of dissociation is by microscopic examination. The dissociation

can be overcome by heating the conglomerate above the temperature of the beginning of dissociation and then quenching. When heated to different temperatures and then quenched, we can easily determine the temperature at which dissociation begins by examination. If this is carried out for a series of conglomerates of slightly different compositions, we can obtain the temperature-concentration curve, the saturation curve on which dissociation begins. The greater the solubility changes with the temperature, the easier is the determination of dissociation. Since this phenomenon of dissociation is observed relatively seldom, obviously the solubility as a rule changes very little with the temperature, or dissociation escapes observation since it takes place so slowly.

Examples of this kind of dissociation will be found in the alloys of Ni-Si, Ag-Sn, Fe-Au, Cu-Sn, and Cu-Zn.

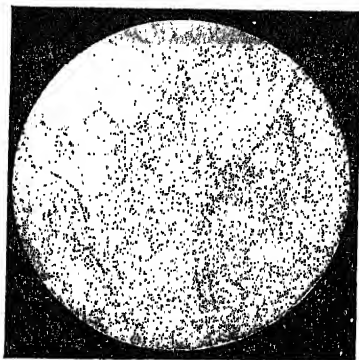


FIG. 122

22% Sn, 78% Ag. Quenched from 490-500°, after slow cooling. Etched with $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$. $\times 68$.

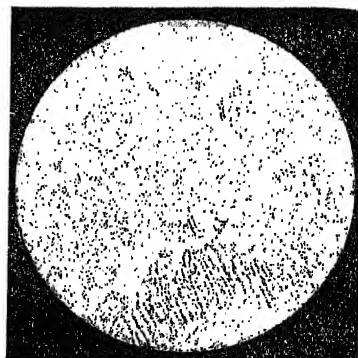


FIG. 123

25% Sn, 75% Ag. Cooled very slowly to 200°. Etched with $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$. $\times 68$.

(a) The Ni-Si alloys (W. Guertler u. G. Tammann, *Zeitschr. f. anorg. Chem.* 49, 93 (1906)) with 0-11.6 per cent. silicon, judging from the thermal phenomenon at its crystallization, must consist of homogeneous crystallites. If these alloys are quenched from a temperature of 1000°, the results agree as expected. If cooled as slowly as possible, one will see on thin polished surfaces dark polygons separated by fine bright lines. This bright constituent corresponds to a solid solution with 27-28 atomic per cent. of silicon, while the darker etched polyhedron surfaces consist of nearly silicon-free nickel. Intermediate stages of dissociation can be observed by quicker cooling.

(b) The Ag-Sn alloys (J. Petrenko, *Zeitschr. f. anorg. Chem.* 53, 200 (1907)) with 17-27 per cent. by weight of tin crystallize on slow-cooling, like those with 0-17 per cent. tin, as homogeneous solid solu-

tions. The crystallization of the alloy with 27 per cent. tin is complete at 480° . Fig. 122 shows the completely homogenous structure of an alloy with 22 per cent. tin cooled slowly to 490° and then quenched. If slowly cooled from 490° , the dissociation of the homogeneous crystallites appears as bright, finely arranged needles (Fig. 123) of the compound Ag_3Sn , which collect as wide borders at the original boundaries of the crystallites.

(c) The Fe-Au alloys with 65-85 per cent. by weight of gold (E. Isaac u. G. Tammann, *Zeitschr. f. anorg. Chem.* 53, 291 (1907)). Fe and Au form two series of solid solutions; in the gold-rich series, the solubility of Fe in crystallizing Au at 1170° amounts to 37 per cent. of Fe, but decreases considerably with diminishing temperature

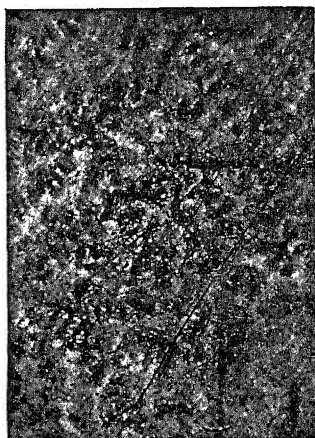


FIG. 124

30% Fe, 70% Au. Etched with HNO_3 1:20. $\times 70$.

so that the solubility of Fe in Au at 400° amounts to only about 20 per cent. of Fe. Consequently a distinct visible dissociation of the gold-rich solid solution appears at diminishing temperatures. This dissociation appears at low magnification as a brown coloration of solid solution. In Fig. 124 one sees "Halos" around the dark the iron rich solid solution which contains about 20 per cent. of gold; these appear to be the unetched patches of gold-rich solid solutions containing 80 per cent. of gold. At larger magnification we can distinctly recognize that the "halos" are produced from needles of the solid solution containing 20 per cent. of gold.

(d) With the Cu-Zn alloys, two miscibility gaps are observed (Shepherd, *Journ. Phys. Chem.* 8, 421 (1904)) which increase with diminishing temperature. The limits of the one shift with increasing temperature from 30-37 per cent. zinc at 910° to 37-45 per

cent. zinc at 400° , since the solubility of zinc decreases in the copper-rich solid solution with diminishing temperature. With the other miscibility gap the solubility of copper and of the zinc decreases with increasing temperature. See the equilibrium diagram of the copper-zinc alloys on page 262. For the miscibility gaps consult page 259.

An appreciable increase of solubility of NiAl in crystallized nickel at diminishing temperatures was established by A. Gwyer (*Zeitschr. f. anorg. Chem.* 57, 137 (1908)).

2. Reactions Caused by Polymorphic Transformations of a Component.

The transformation spreads out from transformation centers which form in the crystallites at the transformation of a crystallizing conglomerate. As these new crystallites grow they intersect each other in irregular planes. It is possible by suitable etching to show two polygonal networks on the polished surface of a conglomerate in which a transformation has taken place; the one is due to that of the boundaries formed on solidification, the second, to the crystallite formed on the transformation. With iron there are found two and sometimes three such networks, while with nickel and cobalt this transformation is still more evident.

The transformations caused by the phenomenon of dissociation in conglomerates of solid solutions stand out clearer than in the pure metals; however that is not always true. Dissociation following transformation are observed only in the series of solid solutions of iron and carbon, and nickel and silicon.

The transformation points of the ferromagnetic metals occur at the following temperatures:

Iron	Cobalt	Nickel
768°	1150°	350°
903°		
1410°		

In a series of 31 solid solutions which these three metals form with each other, detectable dissociation occurs owing to the transformation of ferromagnetic metals with only those indicated by + in the table on page 196. For those indicated by 0 the dissociation cannot be verified, although if the transformation took place in these solid solutions it could be detected either by appearance of the thermal effect or by the determination of the temperatures of the losses and recurrences of their magnetic properties.

The fact that the transformation of ferromagnetic solid solutions in the majority of cases in which it is caused by the transformation of the ferromagnetic solvent, is accompanied with no perceptible dissociation, permits of two interpretations. It can be assumed that the magnetic solid solutions below the temperature of transformation are

TABLE 23

Fe-C	+	—	Ni-C	?	
Fe-Si	0	Co-Si	0	Ni-Si	+
—		Co-Sb	0	Ni-Sb	0
Fe-Sn	0	Co-Sn	0	Ni-Sn	0
Fe-Al	0	Co-Al	0	Ni-Al	0
Fe-Cu	?	Co-Cu	0	Ni-Cu	0
—		—		Ni-Ag	0
Fe-Au	0	Co-Au	0	Ni-Au	0
Fe-Zn	0	—		—	
Fe-Cr	?	Co-Cr	0	Ni-Cr	0
Fe-Pt	0	—		—	
Fe-Mn	0	Co-Mn	0	Ni-Mn	0
Fe-Ni	0	Co-Ni	0	—	
Fe-Co	0	—		—	

supersaturated, since the rate of dissociation at the concerned temperature is quite small. Also the view can be taken that the curves of the loss and recurrence of the magnetic susceptibility of the series of solid solutions of magnetic crystals are actually equilibrium curves and that since both curves coincide, the dissociation will not be observed.

The lack of the phenomenon of dissociation at the transformation of ferromagnetic solid solutions, in case it does not occur by separation of a compound, as in iron carbide, is probably due to certain conditions which occur at the given equilibrium. These conditions are that the lattices of γ - and β -Fe are of the same kind and the distance of the lattice points differ very little. The same applies for the lattices of β - and α -Co as well as for β - and α -Ni.

With the other solid solutions, as with those of many salts referred to in the investigations of Roozeboom (KNO_3 - TiNO_3 , C. van Eyk, *Zeitschr. f. phys. Chem.* 30, 430 (1899); NaNO_3 - KNO_3 , NaNO_3 - AgNO_3 , Hissink, *ibid.*, 32, 537 (1900); HgBr_2 - HgI_2 , Reinders, *ibid.* 32, 494 (1900)), the transformation as a rule is accompanied with appreciable phenomena of dissociation, which takes place in perceptible temperature intervals. Fig. 125 represents the type of a transformation of a component in a series of solid solutions. The substance *B* has a transformation point at the temperature t_2 . This transformation appears in the whole series of B-rich solid solutions which are isomorphous, but while it proceeds to completion at a definite temperature for the pure substance *B*, it requires a temperature interval for the solid solutions. The proceeding of the transformation is in this respect and even in other respects very similar to that of the crystallization of a series of solid solutions with a miscibility gap (Case 7, p. 162). The curves of the dissociation *f b* and of the beginning of the transformation $t_2 b$ intersect at the eutectic point *b*. This solid solution is saturated and is accordingly in equilibrium at the temperature of the point *b* with the solid solution *c* as well as with the solid solution *a*. The dissociation at *a* and *c* takes place at constant temperature. Thus an arrest occurs on the cooling curve which

is found in all alloys which contain solid solution b . The duration of arrest has its maximum value at the point b and disappears at the points c and a . The composition of the three solid solutions which participate in the reaction proceeding at constant temperature are determined by the points b , c and a . When the position of the points d , e and f , which the analogous reactions determine at crystalliza-

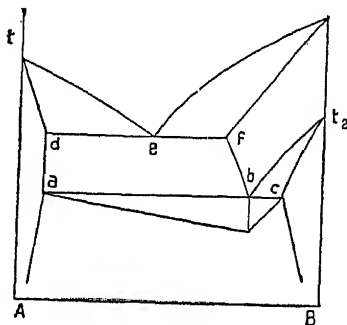


FIG. 125

tion, is known—it is possible to derive these points from the duration of arrests—then the principal part of the equilibrium diagram is established. Then the curves of the equilibrium of two phases: two crystalline varieties, or a melt and a crystalline variety, must pass through these points.

If both components of a continuous series of solid solutions have transformation points it will be expected that their solid solutions will have transformation intervals. The temperatures of the beginning and completion of these intervals occur on two curves which connect both transformation points of the components. An unexpected exception to this rule appears with the Ni-Fe solid solutions (p. 255).

When only one of the two components A of a continuous series of solid solutions, shows a transformation point, then it is not possible for the transformation to appear in the entire series, since a certain excess of the component B will suppress the transformation of the component A . Thus one can observe the transformation of AgI in its solid solutions with AgBr only in the solid solutions from 0.0 to 0.71 mole of AgBr; a greater amount of AgBr suppresses this transformation. (*Zeitschr. f. anorg. Chem.* 91, 263 (1915).)

3. The Formation and Dissociation of Compounds.

It is possible that some molecules are held in the space lattice with such force that they are prevented from entering into chemical reactions. It has been shown, however, that when the formation or dissociation of compounds occur in the anisotropic state, that it takes place according to the linear crystallization rate since it is only limited

by the amount of heat flowing; these reactions produce arrests on the cooling curves.

In a solid solution of the composition of the compound forming from it, the conditions for a rapid reaction are as favorable as possible, since the molecules which form the compound are found side by side. Accordingly if at a definite temperature a change in the stability for the compound and the solid solution of similar composition appears, i.e., where the curves of the partial pressures of the components or the analogous curves of their thermodynamic potentials intersect, we would expect a rapid formation or dissociation of the molecules of a compound.

Magnesium and cadmium form a continuous series of solid solutions (Fig. 126); the temperature interval of crystallization of the series is diminished considerably at 81 per cent. Cd, corresponding to the

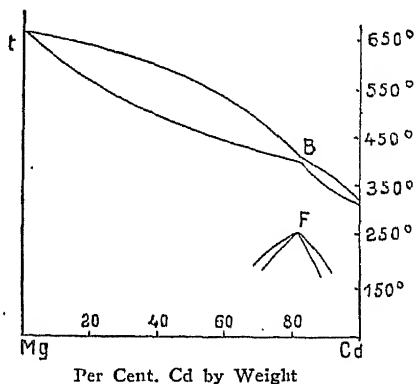


FIG. 126

composition of the compound MgCd (G. Grube, *Zeitschr. f. anorg. Chem.* 49, 72 (1906)). One may then assume that the molecules of the compound MgCd are isomorphous with those of magnesium and cadmium. On the cooling curve of the alloy with 81 per cent. cadmium, a distinct arrest is found at 248° , point F . On the cooling curves of some magnesium- and some cadmium-rich alloys, interval-like retardations are found, which fall between two lines diverging from the point F . One may accordingly assume that in the molecules of the compound separated from the melt, a polymerisation or isomerisation takes place and in consequence, it possesses another space lattice.

A transformation occurs in the solid solutions of the iron-platinum alloys (Isaac u. Tammann, *Zeitschr. f. anorg. Chem.* 55, 63 (1907)). At 1280° an arrest is found on the cooling curve of an alloy with 80 per cent. platinum, which can readily be traced to the formation of the compound FePt , which contains about 80 per cent. platinum. The position of the arrests and of the beginning and completion of

the transformation is indicated in Fig. 127. Both of these curves show the arrest at higher temperatures with increasing platinum content.

In the nickel-rich portions of the nickel-iron solid solutions, the curve for the loss of magnetism with increased temperatures has a distinct maximum (Guertler u. Tammann, *Zeitschr. f. anorg. Chem.* 45, 205 (1906)), which lies at the concentration corresponding to the formula Ni_2Fe (Fig. 165, p. 255). However, it cannot be affirmed that it is a question of the formation of the molecule Ni_2Fe in the solid solution, since this transformation occurs with the loss of ferromagnetism in all solid solutions from pure nickel up to alloys with 33 per cent. nickel. Hence the transformation of the solid solution of the composition Ni_2Fe can be considered as a result of the transformation of nickel.

The dissociation of the members of a series of solid solutions into crystals of two compounds has also been observed (Sander, *Zeitschr.*

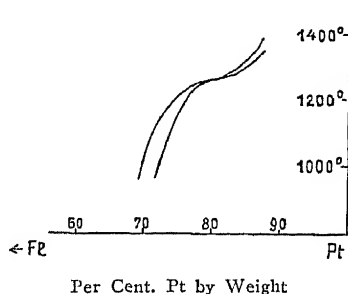


FIG. 127

f. anorg. Chem. 75, 97 (1912)). Antimony and paladium form a series of solid solutions with 58 to 62 per cent. Pd. An arrest occurs at 528° on the cooling curve of the solid solution with 59.6 per cent. Pd, whose composition corresponds to the formula Pd_5Sb_3 . In the solid solutions with more than 59.6 per cent. Pd, the evolution of heat will be accompanied by the formation of bright and dark lamellae (Fig. 128). The bright lamellae are a solid solution with 68.5 per cent. Pd and the dark lamellae are the compound Pd_5Sb_3 . An evolution of heat, accompanied by the dissociation of the original homogeneous solid solution into lamellae of different compositions appears even in the solid solutions with less than 59.6 per cent. paladium. The compositions of the lamellae formed here correspond to the formulae Pd_5Sb_3 and PdSb . The formation of the molecules Pd_5Sb_3 in the original homogeneous solid solutions may be suspected as the cause of dissociation of the solid solutions of 58 to 62 per cent. Pd.

The formation of a new crystalline variety from two existing, upon cooling will be pursued closer microscopically and thermally in the following three cases.

Thallium and antimony crystallize from their liquid mixtures without dissolving any appreciable amount of one another (Williams, *Zeitschr. f. anorg. Chem.* 50, 127 (1906)). The crystallization is completed at 195° ; 8° lower, however, there appears in the cooling curve an unexpected arrest, which has its maximum duration at the

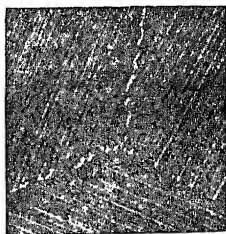


FIG. 128
60% Pd, 40% Sb. $\times 68$.

composition, which corresponds to the formula SbTl_3 . This arrest is quite appreciable in all mixtures. Accordingly it is assumed that antimony and thallium crystallites combine to the compound SbTl_3 . Since the compound contains 3 per cent. by weight of thallium more than the fine grained eutectic, almost the entire eutectic of the

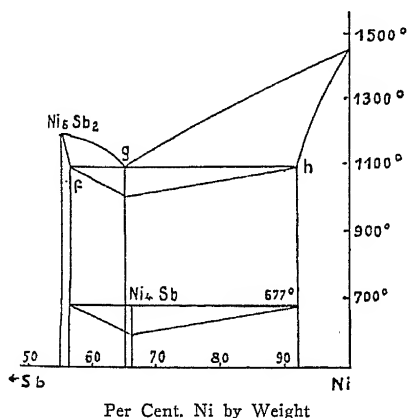


FIG. 129

remainder of a lower antimony content can change into the compound SbTl_3 . Microscopic investigation shows the existence of straw-yellow masses, whose amount changes parallel with the duration of arrest in the alloys of different composition.

Nickel with antimony form a series of solid solutions in which the antimony is dissolved up to 8 per cent. On the other hand the

antimony-nickel compound Ni_5Sb_2 also forms solid solutions, which can dissolve up to 1.5 per cent. nickel. The crystallization of the concerned liquid mixtures is represented in Fig. 129 (Lossew, *Zeitschr. f. anorg. Chem.* 49, 58 (1906)). At 1100° the nickel-antimony alloys consist of a mixture of two saturated solid solutions, *f* and *h*. At 677° an arrest occurs on their cooling curves, whose maximum duration lies at 66 per cent. nickel. The compound Ni_4Sb corresponds to a nickel content of 66.14 per cent. On the basis of the thermal phenomena, we can conclude that at 677° , the following reversible reaction takes place: $x.f + y.h \rightleftharpoons \text{Ni}_4\text{Sb}$.

Microscopic investigation has confirmed this supposition. If we quench an alloy of the eutectic composition of 65.2 per cent.

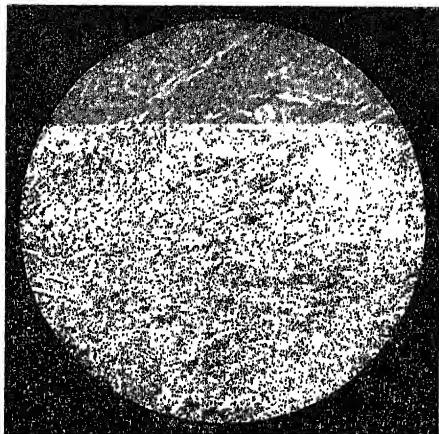


FIG. 130

65.21% Ni, 34.79% Sb. Quenched. Etched with HNO_3 . $\times 190$.

nickel, thus preventing the formation of the compound Ni_4Sb , the alloy will contain a pure eutectic structure (Fig. 130). If cooled slowly, a mass is obtained consisting of homogeneous crystallites, in which only a minute amount of the solid solution *f* is enveloped (Fig. 131). The circumstance, that the compound is only a little richer in nickel than the eutectic *g* and that the eutectic is very fine-grained, is very favorable to the formation of the compound in the eutectic. Fig. 132 shows, that in an antimony-rich alloy, the solid solution *f* is surrounded by a border of the compound Ni_4Sb . Since the crystallites *f* have participated in the reaction, the dark residue, which surrounds the borders, is richer in *f* than the eutectic.

A very similar reaction is observed in the nickel-tin alloys between 60 and 85 per cent. nickel (Voss, *Zeitschr. f. anorg. Chem.* 57, 34

(1908)). With these alloys, the following equilibrium exists at 855° :
 $\text{Ni}_4\text{Sn} \rightleftharpoons x\text{Ni}_3\text{Sn} + y.t$, where t indicates the solid solution with
 15 per cent. tin. By cooling, Ni_4Sn forms; with increasing tempera-

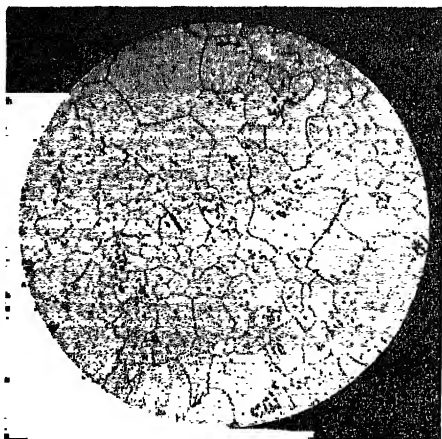


FIG. 131

65.21% Ni, 34.79% Sb. Cooled very slowly. Etched with HNO_3 . $\times 190$.

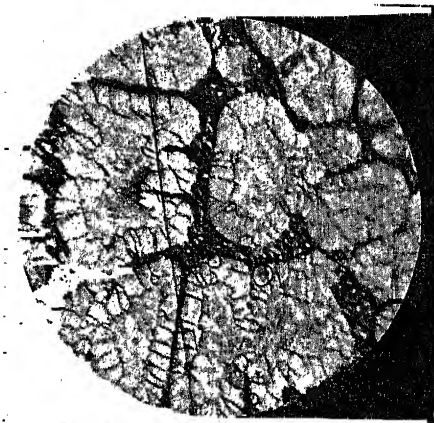


FIG. 132

60% Ni, 40% Sb. Etched with HNO_3 . $\times 145$.

ture, the Ni_4Sn dissociates into the two crystalline varieties, Ni_3Sn and t . The formation of Ni_4Sn is more difficult to complete than that of Ni_4Sb .

The compounds SbTi_3 , Ni_4Sb and Ni_4Sn are exothermic. It is pos-

sible, however, to form endothermic compounds from two crystalline varieties. In contrast to the exothermic compounds, which form during the fall of temperature, the endothermic form with rising temperature.

The compound Ni_3Sn breaks up on cooling into Ni_3Sn_2 and Ni_4Sn . By heating it forms again from the two crystalline varieties. At 837° , the following equation occurs:

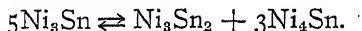


Fig. 133 shows the homogeneous crystallites of the stable compound Ni_3Sn above 837° , and Fig. 134 shows the dissociation of



FIG. 133

60% Ni, 40% Sn. Cooled rapidly.
× 180.

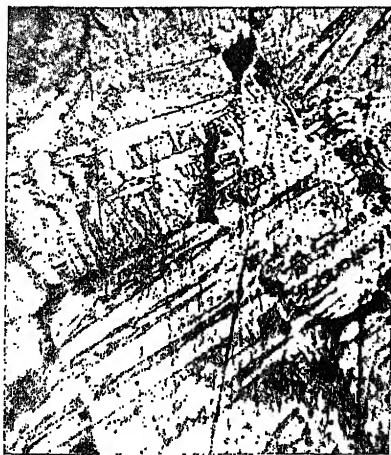


FIG. 134

60% Ni, 40% Sn. Cooled slowly.
× 180.

the homogeneous crystallites upon slow cooling into needles and lamellae of two crystalline varieties.

In the nickel-silicon alloys (Guertler u. Tammann, *Zeitschr. f. anorg. Chem.* 49, 93 (1906)) with 33.3 to 50 atomic per cent. of silicon (19.2 to 33.2 per cent. by weight) the formation of the compound Ni_3Si_2 takes place on cooling due to the dissociation of the solid solution at the temperature of the line hi (Fig. 135) into $\text{Ni}_2\text{Si} + \text{Ni}_3\text{Si}_2$. At the temperature of the horizontal ik , the saturated solid solution i with the crystallites of the compound NiSi form the compound Ni_3Si_2 . Since we can imagine the atomic formation of the solid solutions of the series hi from the molecules of Ni_2Si and NiSi we can consider the reactions proceeding on the lines hi and ik as leading to the same reaction, the formation of Ni_3Si_2 molecules from the molecules of Ni_2Si and NiSi . This reaction-equation can also be

deduced from the duration of the arrest, which appears at the temperature of the lines $h i$ and $i k$. In the homogeneous crystallites of the series $h i$, obtained by rapid cooling, bright needles of Ni_3Si_2 formed by slow cooling appear (Fig. 136). Similar structures are obtained for the cobalt-silicon alloys (Lewkonja, *Zeitschr. f. anorg. Chem.* 59, 331 (1908)), with the same composition, in which the compound Co_3Si_2 forms from Co_2Si and $CoSi$ upon cooling.

The frequent occurrence of the rapid transformations without changing the chemical composition in the so-called solid state, shows that the molecules are somewhat mobile in the space lattice. Since

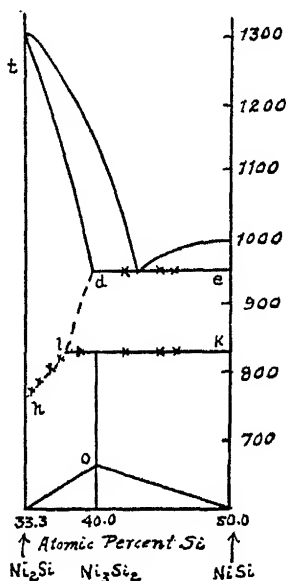


FIG. 135

with these reactions—polymorphic transformations—two molecules of the same substance often combine, the occurrence of rapid reactions in one or even between two crystalline varieties is not so remarkable as it would appear from the standpoint of the old conception, which considered solid bodies as rigid structures.

If the rate of diffusion of the anisotropic molecules of a substance into the crystal of another substance is sufficiently great, their reactivity is not hindered by the fact that they are anisotropic. In any case this is applicable to metallic substances with which this investigation is concerned.

We can obtain identical alloys, which as a rule are produced by the fusion of metals and then cooling of the resulting melt in other

ways, such as by mixing pulverized metals, and then compressing and heating to a temperature at which no melting appears, but where the rate of diffusion is very considerable. The same constituents form as those obtained from fusion, although much longer time is re-

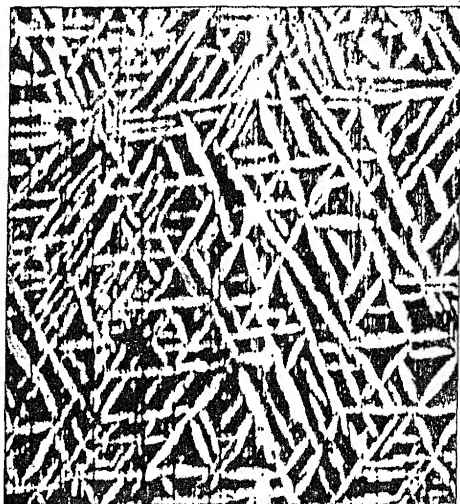


FIG. 136

34.6 atomic per cent. Si, 64 atomic per cent. Ni. Cooled slowly. $\times 70$.

quired. Alloys of the same composition produced by the two ways are readily distinguished by their structure. This experiment shows then, that the atoms of metals are not hindered in their reactivity by the state of anisotropy.

4. Conglomerates Obtained by the Heating of Compressed Pulverized Metals.

The question of whether the pressure used in the formation of an alloy really increases the rate of diffusion of compressed metals and thereby gives an opportunity for the formation of compounds, which are characteristic for many of the alloys obtained through the fusion of the components, has been raised by W. Spring (*Berl. Ber.* 15, 1 (1882)). In the discussion of this question, there are three methods for consideration: microscopic, the thermal and the determination of the electrical resistances.

If the filings of two metals, as zinc and cadmium or copper and silver which form neither compounds nor solid solutions, are mixed in the proportion of their eutectics and compressed under a pressure of 4000 atmospheres, the heating curve of this compressed material

will show a retardation at the eutectic temperature and at some 10 to 30° higher according to the rate of heating, the fusion is completed by the solution of the larger pieces of material. Thermally the alloy obtained by fusion does not differ essentially from the alloy obtained by compressing the pulverized components. The structure for both kinds of alloys consists of small compact alternating layers of zinc and cadmium or silver and copper. However, the structure of the eutectic obtained by fusion is lamellar while the conglomerate obtained by compression consists of irregularly distributed grains of both metals. In the former the crystallites of the lamellar eutectic are rounded off, while in the compressed material the grains of each appear on a polished surface with sharp edges (Figs. 137 and 138).



FIG. 137

72% Ag, 28% Cu. Melted. Etched with $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$. $\times 250$.



FIG. 138

72% Ag, 28% Cu, pressed together. Etched with $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$. $\times 70$.

In cases where the metals form neither solid solutions nor compounds with each other and in the liquid state are quite limited in miscibility, we will find on the heating curve of the compressed material two retardations whose temperatures approach the melting points of the pure metals more closely, the greater the miscibility gap in the liquid state.

If the components form a compound and are miscible in all proportions in the liquid state, but not in the crystalline state, then it would be expected, if the compound does not form by the diffusion of the crystallized metals and only forms in the liquid, that the beginning of the melting of the compressed material will be at a eutectic point, which must lie at a temperature below both eutectic points *a* and *b* (Fig. 139), then the equilibrium of both components *A* and *B* with their melt would become an unstable system like the

two eutectic systems *a* and *b*. Such a point has, however, not been found in any case investigated, but the melting always begins first at the temperature of a eutectic point at which the compound is in equilibrium with one of the components and the eutectic melt. Hence it is concluded that at the surface of contact of the crystals of the conglomerate even in the solid state, small amounts of the compound have formed. The heating curve of a compressed material of the composition A_mB_n , if the heat of formation of the compound is disregarded, can have the form E_1 (Fig. 139) in which retardations appear at the temperatures of the three nonvariant equilibria, *a*, *b* and *c*. The duration of the retardations on these curves will depend upon the solubility of the compound and its components in the melt formed. While heating between *b* and *c*, the compound A_mB_n forming will separate from the melt and will melt at *c*. If the heat of formation is considered, then after the beginning of the melting at

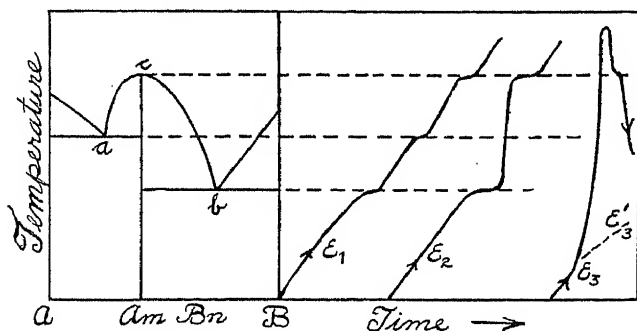


FIG. 139

point *b*, Curve E_2 (Fig. 139), the temperature rises rapidly up to the melting point of the compound at which a perceptible retardation is made, while the retardation at *a* will be concealed through the liberation of the heat of combination. Such cases have been observed by G. Masing (*Zeitschr. f. anorg. Chem.* 62, 265 (1909)) with the following pairs: zinc-magnesium, lead-magnesium, tin-magnesium and bismuth-magnesium. With the antimony-magnesium alloys a heating curve of the form E_3 (Fig. 139) was found. Here the formation of the compound Mg_3Sb_2 in the compressed material produced from antimony and magnesium begins at a perceptible rate even 300° below that of the lowest eutectic point *b*. The temperature rise is then steadily accelerated as shown in the comparison of the course with that of the heating curve E_3' after the end of the reaction (Fig. 139), and then continues to rise above the melting point of the compound *c* and finally diminishes rapidly after a retardation at the melting point of the compound.

When the components form a continuous series of solid solutions,

it will be found upon rapid heating of a compressed material, that a retardation of the temperature rise at the melting point of the component *A* takes place as indicated on the heating curve E_1 (Fig. 140). The further course of the heating curve will be determined by the rate of diffusion of the components *A* and *B* into each other and by the rate of heating. If the rate of heating is very great and the rate of diffusion very small, a second retardation will be found at the melting point of the component *B*. If the rate of heating is now allowed to diminish, then for greater rates of diffusion these retardations become indistinct, and an interval-like retardation will appear between them corresponding to the formation of solid solutions. That the formation of solid solutions really occurs below the melting points of *A* can easily be shown in the following manner. If a compressed material of the composition of the material which yields the heating curve E_1 is heated a long time at this temperature, then when the

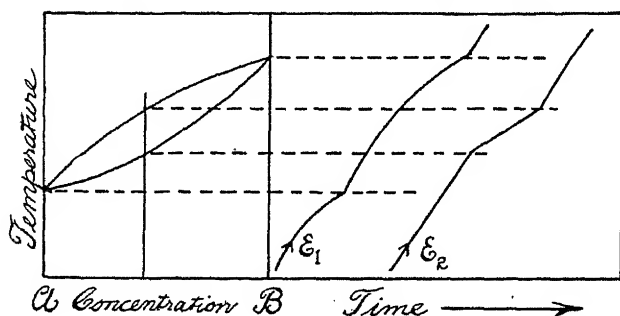


FIG. 140

same concentration has been produced throughout by diffusion, an interval-like retardation must be found on the heating curve E_2 , whose temperatures correspond to the crystallization intervals of this mixture. In this manner it can be shown that compressed material of magnesium-cadmium and also lead-tellurium, where the relations are somewhat modified by a small miscibility gap and by a maximum on the curve of the beginning of crystallization, actually meet the expected relation.

No matter whether the two components form solid solutions or a compound and whether this compound is miscible with the components, the melting of a compressed rod of both components begins at the temperature of the nonvariant equilibrium of two crystalline varieties formed in the compressed material, whose temperature is the lowest. Since at the start of melting, the phases occurring in the concerned nonvariant equilibrium must be present in the compressed material, it follows that if a compound or a saturated solid solution did not exist before heating, this phase must have formed during the heating below the melting temperature.

The reaction which takes place in the compressed material upon heating can also be verified by microscopic investigation. The smallest trace of a solid solution or a compound which will readily form through the fusion of the two components cannot be detected after the material has been compressed under a pressure up to 5000 atmospheres. This general result, which is contradictory to former suppositions, can moreover be confirmed with still greater accuracy in the cases of lead-thallium by determining the electrical resistance of wire produced by compressing the lead and thallium. Although these two metals will diffuse into one another quite rapidly at about 100° the resistance of the wire produced from the filings of both metals agrees with the resistances of the components as calculated according to the law of mixtures. At first the resistance of the wire increases about 10 per cent. in the course of a day, then this increase is retarded somewhat and in the course of a month the resistance is increased about 60 to 75 per cent. Heating the wire to 160° naturally increases the resistance much more rapidly, which fact corresponds to the increasing rate of diffusion. The basis of this phenomenon is the fact that the resistance of solid solutions is always greater than the resistance of the wire as calculated from the resistances of the components according to the law of mixtures.

As mentioned neither traces of solid solutions or of a compound are found immediately after the compression of the unheated particles of both components. If the temperature of the compressed material is raised, the rate of diffusion of the metals increases and we will find at the original boundary surfaces of both components, solid solutions or compounds and in some cases both. These will be found in the form of borders which separate the original existing components from each other. No third crystalline variety is found in a mixture of bismuth and thallium after compressing under 5000 atmospheres at room temperature (Fig. 141). After heating for 5 hours at 120° a blue border forms between the bismuth and the thallium (Fig. 142). If the compressed material is permitted to lie at ordinary pressure and room temperature for one year, then practically the same structure is obtained. The blue border corresponds to a saturated solid solution with 66.3 per cent. Tl (*Zeitschr. f. anorg. Chem.* 51, 330 (1906)). If heated a little longer at 165° a yellow border corresponding to the compound Bi_5Tl_3 forms between the bismuth and the blue border. The formation of solid solutions and compounds therefore takes place at temperatures when the whole is still solid.

If equal amounts of copper and tin filings are compressed together a sharp boundary occurs between the individual grains of copper and tin. If this compressed material is heated at 200° for 16 hours at a temperature a little below the melting point of tin, two layers form between the copper and tin grains; the layer next to copper corresponds to the compound Cu_3Sn and the darker layer next to the tin



FIG. 141

37% Tl, 63% Bi. Pressed together. Etched in air. $\times 70$.



FIG. 142

37% Tl, 63% Bi. Pressed together and heated for $5\frac{1}{2}$ hours at 120° . Etched in air. $\times 70$.



FIG. 143

50% Cu, 50% Zn. Pressed together. Etched with $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$. $\times 120$.



FIG. 144

50% Cu, 50% Zn. Pressed together and heated for 20 hours at 400° . Etched with $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$. $\times 70$.

corresponds to a crystalline variety rich in tin, the composition of which has not been definitely ascertained. According to Heycock and Neville an alloy with 9 to 40 per cent. of copper forms upon fusion of the two metals at 400° .

A similar product is obtained upon compressing together equal amounts of copper and zinc particles. No other constituent exists between the copper and zinc following compression (Fig. 143). However, if this is heated at 400° for 20 hours, a layer of the color of brass surrounds the original particles of zinc (Fig. 144). This brass layer corresponds to the composition of a solid solution with 45 to 48 per cent. of zinc. Near the copper, the brass layer is surrounded by a bright halo which corresponds to a thin layer of copper-rich solid solution with 35 per cent. zinc. Hence it is readily seen that brass is not produced by the compression of copper and zinc alone. Here again the rate of diffusion at room temperature is very low. It is necessary to raise the temperature considerably to produce a noticeable formation of brass by diffusion in the compressed material.

In all of these cases a layer of solid solution or compound is formed by the diffusion of the metals into one another. This layer separates the metals. In spite of this separation, the formation of a compound will extend further by sufficient rate of diffusion. One must then assume that in general the metallic compounds are permeable to their components.

By pressing together two metals at room temperature, a compressed material is obtained which consists only of the pure metals and in which neither compounds nor solid solutions form, although solid solutions form easily upon the fusion of the two metals. Pressure alone does not increase the rate of diffusion of the metals to such an extent that any perceptible amount of compounds or solid solutions will be formed.

The great ability of metals to diffuse into one another at high temperatures makes possible the formation of alloys from mixtures of oxides or other compounds. For example if NiO and CuO are mixed as thoroughly as possible, the mixture reduced in a stream of hydrogen, then compressed and again heated in a stream of hydrogen to a temperature of 800° , a piece of alloy is obtained which can readily be rolled. The two metals are especially intimately mixed, if a salt of two metals, as NiWO_4 , is reduced.

This method is recommended for producing alloys when one or both components are difficult to melt, or when one or both components are volatile.

5. The Diffusion of Two Metals into Each Other.

If the solution of a metal in mercury and pure mercury are stratified so that the less dense liquid is above the other and after a time the concentration of the dissolved metal determined in two layers of known distance apart, the diffusion coefficient D may be deduced from these data. D is the amount in grams which diffuses through a cross section of one sq. cm. per day if the concentration difference per cm. is equal to one.

Such determinations have been made by G. Meyer and Wogen (*Ann. Phys.* 23, 345 (1917)). These investigations showed the value D of metals dissolved in mercury as a periodic function of the atomic weight, the metals with large atomic volume having smaller D values than those with small. Accordingly Li, Na, K, Rb, Cs, Ca, Sr and Ba have smaller D values than Zn, Cd, Sn, Au, Tl and Pb. This is what would be expected if the atoms of the dissolved substance are considered as balls moving in a viscous liquid. On the basis of this assumption, Meyer and Wogen have calculated the D values of metals and compared them with those found. The calculated values for the metals of the alkali and alkaline earth metals and for gold are in good agreement, but those found for Zn, Cd, Sn, Tl and Pb are one to four times larger than those calculated. The first group of metals form compounds with mercury while the second group either do not or they are strongly dissociated in solution.

The diffusibility of metals in the solid state is of considerable interest. It makes possible the welding of one metal to another. For this purpose a layer of the second metal is deposited on the first electrolytically and then annealed. The solid solution layer formed below the temperature of melting can be altered considerably by regulating the heating temperature and time.

The following values have been found for the diffusion coefficients of two solid metals.

Au in Pb		Au in Ag		C in Fe	
100°	0.00002 sq. cm./day	870°	0.000037 sq. cm./day	925°	0.010 sq. cm./day
165°	0.004 "	Fraenkel and Heuten ²		J. Runge ³	
200°	0.7 "				
Roberts-Austen ¹					

The variations in these determinations are not inconsiderable because the solid metals consist of grains that are separated by very thin layers of foreign material and since the thickness and composition of these layers are variable so is also the D value. As a result of this, the diffusion boundary of carbon in iron is not a plane but a toothed surface.

If a small, smooth piece of iron be heated in a mixture of hydrogen and hexane and a section cut vertically to the surface, three zones can be differentiated by suitable etching. (Schönert and Tammann, *Z. anorg. Chem.* 122, 27 (1922)).

The outer zone shows cementite needles and grains in a ground mass of pearlite. The needles are oriented practically vertically to the surface. While a part of these needles are constricted toward the center others maintain the same breadth and break off suddenly. This zone is hyper-eutectic and its breadth is given by the length of the cementite needles.

¹*Proc. Roy. Soc., London*, 59, 283 (1896).

²*Z. anorg. Chem.* 116, 1 (1921).

³*Z. anorg. Chem.* 115, 293 (1921).

The second zone appears entirely homogeneous under a magnification of 50 diameters. At its lower border the first ferrite grains are visible at this magnification. At a magnification of 360 diameters a large amount of iron carbide is visible in the upper portion while in the lower part, ferrite is embedded in pearlite. A concentration decrease of carbon therefore takes place inside of this zone but as a mean it contains 0.9 per cent. of Carbon.

The third zone is hypo-eutectic. Ferrite is primarily precipitated

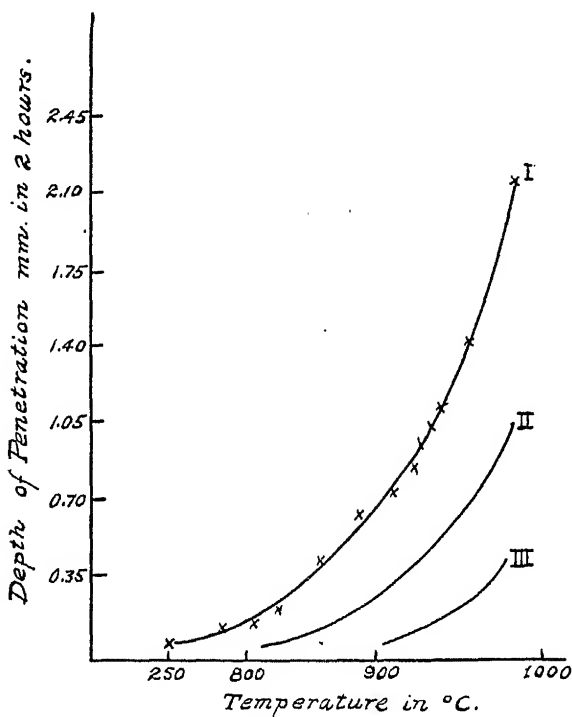


FIG. 145

and surrounded by pearlite the amount of which decreases toward the center. The decrease however is not uniform and the boundary line is not straight but zigzag.

Experiments below 900° show only zones 2 and 3. Fig. 145 shows the depth of penetration in relation to the temperature, curve I gives the depth of the entire carburized zone, Curve II the depth of zones 1 and 2, Curve III that of zone 1.

It is worthy of note that the transition points of iron at 769° and 906° do not appear as breaks in the curves in Fig. 145. This is explained in the following way.

The transition point at 769° , where α changes into β iron, is lowered by the small amount of manganese present. The zone at 750° therefore does not represent the diffusion of carbon into α iron but β iron.

In the field of existence of β iron, diffusion takes place although β -iron dissolves no carbon. The process of diffusion may be conceived as follows. If on the surface of the crystallites of β -iron there exists an excess of carbon, a transition of enough β -iron into γ -solid solution takes place to bring about equilibrium between β -iron and γ -solid solution at the given temperature.

This equilibrium depends on the temperature; at 770° the γ -solid solution contains 0.4 per cent. C, at 850° 0.2 per cent. C. Due to the continuous diffusion of the carbon into the γ -solid solution, its concentration is increased and the equilibrium zone is displaced toward the center. In the β -iron field there must be a sharp boundary between the carbon-free β -iron and the outer zone of γ -iron containing carbon. Such a boundary is observed especially in the experiments at 750° - 850° . Between 850° and 900° it is not so prominent.

In the field of existence of β -iron then the observations are really made on diffusion in γ -iron. With increasing temperature the equilibrium zone between β -iron and γ -solid solution is displaced toward smaller carbon concentration up to 906° where it reaches a point where all the β -iron is transformed into γ -iron. There is therefore no break in the curve (Fig. 145) at this point.

E. The Relation of Metals in Binary Mixtures

The explanation of the relation of chemical elements, the greater number of which are metals, to each other is one of the principal subjects of inorganic chemistry. Since the time of Berzelius investigations have been in progress regarding the relation of the metalloids to metals and the relation of the binary compounds to each other. With the introduction of electric heating, investigations have been made concerning the relation of carbon to metals. In general it is almost impossible to explain comprehensively and exhaustively the ability of the elements to form compounds with each other. The method for solving this problem is still unknown.

The first useful work appeared concerning the mutual relations of metals only after the theory of the heterogeneous equilibrium had been developed and the difficulties of measuring high temperatures had been overcome.

Bakhuis Roozeboom, Roberts-Austen, Heycock and Neville, and Kurnakow, with the aid of their students, made the first step in this direction. Pfaundler and Roozeboom made studies of the equilibrium of salt-hydrates and their solubility. Their method had to be modified, however, in its application to alloys. They gave almost their entire attention to the beginning of crystallization and ignored the phe-

nomena at the completion of crystallization. This fault was remedied by the development of thermal analysis following which, the determination of the composition of the compounds and of the saturated solutions was undertaken in a manner more exacting than formerly.

The relation of two substances to each other is completely explained by the equilibrium diagram in a manner much shorter and clearer than was previously possible. The fact must not be overlooked that what the equilibrium diagram expresses concerning the ability of the elements to combine refers to the temperature interval in which the two elements are investigated. If we mix, for example, liquid N_2 and O_2 and on the basis of the cooling curve determine their equilibrium diagram at temperatures below their critical temperatures, we will conclude that O_2 and N_2 do not form any compounds. This result is, however, only correct for the temperature interval investigated, and erroneous if applied at high temperatures. In analogy to this example it would be possible for two metals such as Bi and P or Bi and Sn which form no compounds upon heating their liquid mixtures to a temperature 100° above the melting points of the components, to form compounds if their mixtures or mixtures of their vapors were further heated to higher temperatures. Regarding the two examples mentioned, it is true that there is no evidence after heating the liquid mixtures to 1500° , which would indicate the formation of a compound at higher temperatures.

These limitations, however, do not concern the method itself. For if the molecules of a compound form in the liquid mixtures after heating strongly and separate in the form of crystals upon cooling, their separation could not escape detection by thermal analysis.

There is, however, still a second limitation of the results obtained which requires the consideration of the equilibrium diagram in a more careful manner. Thermal analysis naturally can give us information only of the kinds of molecules in the liquid mixtures which form crystals. The molecular varieties which transform at the process of crystallization into the crystal forming molecules are not indicated by thermal analysis, since it follows only the process of liquid mixtures becoming heterogeneous. It can as a rule, however, be stated that the stable molecular varieties form crystals, and that the unstable molecular varieties, of which there are many existing in the melt, disappear upon crystallization. In general the thermal analysis establishes only the existence and composition of the stable crystal-forming molecules. The complete analysis of all the kinds of molecules present in liquid mixtures requires an unusually complete detailed knowledge of the properties of liquid metal mixtures at high temperatures. Such comprehensive information is not ordinarily at our disposal.

Even the investigation of the mutual relations of elements with the aid of thermal analysis not infrequently meets difficulty due to the scarcity of a number of elements or to the difficulties of obtaining

them in the metallic state. In such cases the normal amount of 20 grams can be greatly reduced for the determination of a cooling curve. It is even possible with the use of very fine wires as thermal elements and very thin protecting tubes for the thermal elements to obtain a distinct cooling curve with an amount of one gram (*Zeitschr. f. anorg. Chem.* 67, 183 (1910)). Sometimes a still smaller amount is sufficient in the investigation of rare elements, as gallium, germanium and indium, although these elements are easily reduced from their oxides. It is more difficult to procure material when the oxides are hard to reduce, especially if the concerned metal is not only rare but reactive as is the case for some of the rare elements.

If the boiling point of one of the elements lies at a temperature below the melting point of the other element, then the melting together of the two elements can only be undertaken under high pressure. As this process involves a pressure-resisting container, such pairs of metals have not as yet been completely investigated. A beginning in this direction has been made in the alloys of zinc and iron (*Zeitschr. f. anorg. Chem.* 83, 257 (1913)).

While there are still a very considerable number of the binary mixtures of elements to be investigated there is a large amount of material available on the relations of the elements to each other.

It will be impossible for us to consider here the equilibrium diagrams of all pairs of metals which have been investigated. However such a collection was started by K. Bornemann (*Die binären Metalllegierungen* I. u. II (1909 and 1912)) and was nearly completed in a rather critical manner.

The greater portion of the original work is to be found in the *Zeitschrift für anorganische Chemie*, 1904 to 1913.

The results of the equilibrium diagrams of the pairs of metals investigated can only be considered in an abbreviated form. Consequently the following viewpoints will be considered:

1. The tendency of metals to combine. This property is particularly important for the metals, because a large series of metals form no compounds with each other, while on the other hand many metals form more or less numerous compounds.
2. The formulae of these compounds are of especial interest from the standpoint of the doctrine of valency, since the conditions here are the simplest, being binary compounds of two elements.
3. It is of considerable importance whether two metals in the liquid state are or are not miscible in all proportions. When the two liquid metals do not, or at most only scarcely dissolve at the melting point of the highest melting metal, they will generally crystallize almost unaltered from the two liquid layers. This relation was previously indicated by the remark "the two metals form no alloys."
4. Finally the ability of two metals or their compounds in the anisotropic state to form solid solutions with each other, is of the

greatest importance since practically all alloys which permit cold working consist exclusively of solid solutions. The knowledge of the concentration of the end members of the series of solid solutions is therefore of importance. It is always detrimental for a crystal to form from a liquid which contains foreign matter, as the foreign matter is absorbed, even if only in traces. Practically, however, the solubility of foreign matter in the crystals may frequently be disregarded.

In the following table the main points of the general relations of the metals to each other are noted by the following abbreviations.

- f* - Solubility in the liquid state in all proportions.
- fL*, Miscibility gap in the liquid state.
- K*, Continuous series of solid solutions.
- KL*, Gap in the series of solid solutions.
- O*, No chemical compound.

If two metals form compounds with each other, the formulae of their compounds are given. If the composition of the compound cannot be stated with certainty, then its existence is noted by the letter *X* or *Y* as with iron-tin, iron-chromium and lead-platinum.

The limit of concentration (per cent. by weight) of the miscibility gap in liquids and in the anisotropic state are noted by the sign *fL* and *KL* with the figures.

For example, bismuth-aluminum with symbols: *fL* 3.7-98.9 Bi, *KL* 0-100 Bi, *O*, means that bismuth and aluminum are slightly soluble in each other at the melting point of the higher melting metal and the miscibility gap at this temperature extends from 3.7 to 98.9 per cent. by weight of bismuth. Crystallizing bismuth is not able to dissolve any perceptible amount of aluminum and crystallizing aluminum no bismuth. A crystalline compound of the two metals does not separate from the melt.

Data for 20 metals concerning the miscibility in the liquid state as well as the solid anisotropic states is compiled in Table 24. Table 25 contains data for the same metals regarding their ability to form compounds. Besides these two principal tables, two secondary tables trace out the metals which possess considerable ability to form compounds such as lithium, sodium, potassium, rubidium, caesium, calcium and cerium and also the metalloids, phosphorus, arsenic, sulphur, selenium and tellurium. These secondary tables (Tables 26, 27, 28 and 29) likewise contain data regarding the ability to form compounds and the miscibility gaps in the liquid and crystallized states.

REMARKS ON TABLES 24 AND 25

1. The formation of the compound AlSb does not result immediately.
2. By the addition of cobalt, the melting point of cadmium is lowered about 6°. The completion of the diagram is prevented by the volatility of cadmium.
3. The attempt to produce cadmium-chromium alloys fails because at 650° the chromium will not be moistened by cadmium.

TABLE 25. FORMULÆ OF METALLIC

	Ag	An	Mg	Zn	Cd	Hg	Al	Tl	Sn	Pb
Cu	o	o	$\frac{\text{CuMg}_2}{\text{Cu}_2\text{Mg}}$	$\text{Cu}_2\text{Zn}_3^*)$	$\frac{\text{Cu}_2\text{Cd}^?}{\text{Cu}_2\text{Cd}_3}$	CuHg	$\frac{\text{Cu}_3\text{Al}}{\text{CuAl}} \frac{\text{CuAl}}{\text{CuAl}_2}$	o	Cu_3Sn	o
Ag		o	$\frac{\text{AgMg}}{\text{AgMg}_3}$	$\frac{\text{Ag}_3\text{Zn}_2}{\text{AgZn}} \frac{\text{Ag}_2\text{Zn}_3}{\text{Ag}_2\text{Zn}_5}$	$\frac{\text{AgCd}_4^?}{\text{AgCd}_3} \frac{\text{Ag}_2\text{Cd}_4^*)}{\text{AgCd}}$	$\text{Ag}_3\text{Hg}_4^?$	$\frac{\text{Ag}_3\text{Al}^*)}{\text{Ag}_2\text{Al}^*)}$	o	Ag_3Sn	o
Au			$\frac{\text{AuMg}}{\text{AuMg}_2} \frac{\text{AuMg}_3}{\text{AuMg}_5}$	$\frac{\text{AuZn}}{\text{Au}_3\text{Zn}_5} \frac{\text{AuZn}_8}{\text{AuZn}_8}$	$\frac{\text{Au}_4\text{Cd}_3}{\text{AuCd}_3}$	$\frac{\text{Au}_2\text{Hg}_3}{\text{Au}_3\text{Hg}}$	$\frac{\text{Au}_4\text{Al}}{\text{Au}_5\text{Al}_2} \frac{\text{Au}_3\text{Al}}{\text{AuAl}} \frac{\text{AuAl}}{\text{AuAl}_2}$	o	$\frac{\text{AuSn}}{\text{AuSn}_2} \frac{\text{AuSn}_4}{\text{AuSn}_4}$	$\frac{\text{Au}_3\text{Pb}}{\text{AuPb}_2}$
Mg				MgZn_2	<u>MgCd</u>	—	$\text{Al}_3\text{Mg}_4^*)$	$\frac{\text{Mg}_3\text{Tl}_2}{\text{Mg}_2\text{Tl}} \frac{\text{Mg}_2\text{Tl}_3}{\text{Mg}_2\text{Tl}_3}$	<u>Mg₂Sn</u>	Mg_2Pb
Zn					o	o	<u>Al_2Zn_3</u>	o	o	o
Cd						o	o	o	$\text{CdSn}_4^?$	o
Hg							—	Hg_5Tl_2	$\text{Hg}_3\text{Sn}^?$	o
Al								o	o	o
Tl									o	$\text{PbTl}_2^?$
Sn										$\text{Pb}_4\text{Sn}_3^?$
Pb										
Sb										
Bi								$\frac{\text{In-Tl}}{\text{o}}$		$\frac{\text{In-Pb}}{\text{o}}$
Mn										
Fe										
Co										
Ni										

* Corresponds to end member of a solid solution series.

Sb	Bi	Mn	Fe	Co	Ni	Pd	Pt	Cr	Si
Cu_2Sb Cu_3Sb	o	o	o	o	o	o	o	o	Cu_2Si $\text{Cu}_{10}\text{Si}_4$?
Ag_3Sb	o	$\text{MnAg}_3^*)$	o	o	o	o	$\text{Ag}_2\text{Pt}^*)$	o	o
AuSb_2	o	$\text{AuMn}?$	o	o	o	o	o	—	o
Mg_3Sb_2	Mg_3Bi_2	—	—	—	Ni_2Mg NiMg_2	—	—	—	Mg_2Si
Zn_3Sb_2 ZnSb	o	o	Zn_7Fe Zn_3Fe (9)	Up to 18.5 Co invest. CoZn_4	NiZn_3 $\text{NiZn}?$ (10)	—	—	X (7)	—
CdSb Cd_2Sb_2 un- stable X?	o	—	X (4)	X? (2)	Up to 18 Ni invest. Cd_4Ni	—	—	? (3)	—
—	o	—	—	—	—	—	—	—	—
AlSb (1)	o	$\text{Al}_3\text{Mn}?$ $\text{AlMn}_2?$	FeAl_3	$\text{Co}_3\text{Al}_{10}$ Co_2Al_6 CoAl	NiAl_3 NiAl_2 NiAl	—	—	AlCr_3	o
Ti_3Sb	Bi_2Ti_3 $\text{BiTi}_2?$	o	? (8)	(5)	o	—	PtTi	—	o
$\text{SbSn}^*)$	$\text{Bi}_2\text{Sn}?$	SnMn_4 SnMn_2 $\text{SnMn}?$	X Y?	CoSn Co_2Sn	Ni_3Sn_2 Ni_7Sn Ni_4Sn	—	SnPt_3 SnPt Sn_2Pt_2 Sn_8Pt_3	o	o
o	$\text{BiPb}?$	o	o	o	o	Pb_2Pd PbPd PbPd_2 PbPd_3 $\text{Pb}_2\text{Pd}_4?$	X PbPt Y	o	o
	o	$\text{Sb}_2\text{Mn}_3^*)$ SbMn_2	Sb_2Fe Sb_2Fe_3	CoSb CoSb_2	Sb_2Ni_4 SbNi Sb_2Ni_5 SbNi_4	Sb_2Pd SbPd Sb_3Pd_5 SbPd_3	PtSb_2 $\text{PtSb}?$ Pt_2Sb_2	Sb_2Cr SbCr	o
		X, Y, Z	o	o	Bi_3Ni BiNi	—	—	o	o
			o	o	Com- pounds	—	—	—	Mn_2Si MnSi
				$\text{Fe}_4\text{Co}_3?$	$\text{FeNi}_2?$	—	o	X (6)	FeSi
					o	—	—	X	Co_2Si Co_3Si_2 CoSi CoSi_2 CoSi_3
						o	—	o	Ni_2Si Ni_3Si Ni_2Si_2 NiSi $\text{Ni}_2\text{Si}_3?$

* Corresponds to endmembers of a solid solution series.

TABLE 26

	Li	Na	K	Rb	Cs	Ca	Ce
Na	fL 3-92 Li KL 0-100 Li		f - KL 0-100 K	—	—	—	—
K	fL 2?-95 Li KL 0-100 Li			—	—	—	—
Mg	f -? KL 5-15 Li?	fL 2-98.4 Na KL 0-100 Na	fL 0-100 K KL 0-100 K	—	—	f - KL 0-100 Ca	f - KL 0-100 Ce
Zn	—	fL 3.9-100 Na KL 0-100 Na	fL 0-97 K KL 0-100 K	—	—	f - KL 0-100 Ca	?
Cd	f - K -	fL 23.4-32.4 Na KL 0-100 Na	fL 6.2-97.2 K KL 0-100 K	—	—	fL 12-64 Ca KL 0-87 Ca	—
Hg	f - KL 0-2.2 & 5-100 Li	f - KL 0-22.5 & 24.0?-100 Na at 20°	f - KL 0-100 K	From 1.4-6.8 Rb invest. f -? KL ?	f - KL 0-10 & 12.5-100 Cs	—	—
Cu	—	—	—	—	—	f - KL 0-10.5 & 13.7 to 56 Ca over 580° 0-10.5 & 13.7-70 Ca under 580°	f - KL 0-100 Ce
Au	—	f - KL 0-100 Na	—	—	—	—	—
Ag	—	f - KL 2-100 Na	—	—	—	f - KL 0-38 & 40.4-100 Ca	—
Al	—	fL 0-100 Na KL 0-100 Na	fL 0-100 K KL 0-100 K	—	—	fL 16-43 Ca KL 0-100 Ca	f - KL 0-100 Ce
Tl	—	f - KL 0-100 Na	f - KL 0-100 K	—	—	f - KL <2-16.6 & 22-66.5 Ca at 692°. <2-16.6 & 22-100 Ca at 20°	—
Sn	f - KL 0-100 Li	f - KL 0-100 Na	f - KL 0-100 K	—	—	Up to 18 Ca invest. f - KL 0-10.1 & about 11->18 Ca	f - KL 0-100 Ce
Pb	—	f - KL 0.5-18.3 20.6-28.9 & 30.8-100 Na	fL 9-35? K KL 0-100 K	—	—	f - KL 0-6.2 7.2-27.9 & 39.3-100 Ca	Up to 60 Ce investigated
Sb	—	f - KL 0-100 Na	—	—	—	Up to 9 Ca investigated f - KL 0-9 Ca	—
Bi	—	f - KL 0-100 Na	f - KL 0-100 K	—	—	Up to 10.1 Ca investigated f - KL 0-10.1 Ca	f - KL 0-100 Ce
Si	—	—	—	—	—	f - KL 0-100 Ca	Up to 70 Ce investigated f - KL 0-70 Ce
S & Te	—	fL 90.6-94.9 Te KL 0-100 Te	—	f ? KL ?	f ? KL ?	—	—

4. The completion of the fusion diagrams is prevented by the great volatility of cadmium.
5. Cobalt is soluble in thallium only up to 2.5 to 3.0 per cent. Molten cobalt can dissolve but 2.87 per cent. of thallium, the excess distills off.
6. KL , depends on the temperature at which the melt is heated. Slow formation of the compound.
7. On account of the distilling of the zinc at high temperatures it is difficult to produce zinc-rich alloys.
8. On account of the volatility of thallium it is not possible to produce alloys at atmospheric pressure.
9. From the structure of alloys produced under pressure.
10. From 0 to 50.4 per cent. nickel extrapolated from the ternary system copper-nickel-zinc according to Tafel.

1. The Characteristics of a Chemical Compound.

The conception of a chemical compound is founded on the atomic basis and does not presume to define the forces any further than those which are effective between the atoms forming the compound. This conception is based on the fact that atoms move together as a complex. This is determined from the vapor-volume. If it is too large it is traced to dissociation and attributes the ability to a portion of the atoms forming the compound, individually or in small complexes to move independently in the presence of the molecules of the compound. Dissolved substances are considered in a similar manner and finally this conception is utilized even for solid bodies, isotropic or anisotropic, in so far as diffusion exists in them. On the other hand the physical basis of this conception disappears in temperature regions where diffusion is not really perceptible and where the atoms only oscillate about the lattice points of their space lattice. Whether the molecules in isotropic glass oscillate as such or whether the heat motion is reconveyed only by oscillations of the atoms is still undecided.

The molecular heat of crystallized compounds is according to F. Neumann and H. Kopp, the sum of the atomic heats of their component elements. This is generally true for metal compounds (see page 277). If the law of Neumann-Kopp holds, there remains very little over for the increase in the energy of the vibrations with temperature increase. Hence the existence of molecules in a crystal is without meaning. If, however, the temperature is raised sufficiently for diffusion the molecular heat of metal compounds becomes greater than the sum of the atomic heat and the conception of the molecules has a meaning.

In what follows the question of characteristics of compounds will be further investigated in the case where the bodies concerned have been formed from binary melts.

In the process of crystallization, a continuous series of mixtures of binary melts can change into crystal conglomerates, which within a certain concentration range, consist of mixtures of two crystalline varieties. A concentration range may follow in which one crystal-

line variety is replaced by another. This process may happen repeatedly. Series of solid solutions do not appear in this case, hence each of the constituents forming as the composition of the melt changes, has a completely definite composition. Such constituents we will call singular.

Now the results obtained from thermal analysis have shown that the compositions of singular constituents always correspond to the law of multiple proportions. Based on this, we can consider such singular constituents as compounds, although proof that their complex atoms (molecules) move independently during diffusion, cannot as a rule be obtained.

From analogy with other substances for which the diffusion of molecules is proven and whose composition is in accordance with the law of multiple proportion, we have made the assumption that all singular crystalline varieties whose compositions agree with multiple proportions are compounds.

The formation of singular crystalline varieties will take place either directly from the melt, in which case a maximum is found on the melting curve of the melt at the same composition as that of the singular crystalline variety, or it will proceed in the manner that a singular crystalline variety separated from the melt of a definite composition at a definite temperature, will form a new singular crystalline variety. The latter manner does not correspond to the law of multiple proportions.

It sometimes happens, however, that the composition of non-singular crystalline varieties, e.g. an end member of a series of solid solutions corresponds to the law of multiple proportions. For example the composition of the end members of the series of solid solutions of zinc-copper from 31 to 40 per cent. copper, with 40 per cent. copper within the limit of error corresponds to the formula Zn_3Cu_2 , and the end members of the series of the solid solutions of iron-silicon correspond to the formula Fe_2Si . With manganese-antimony more series of solid solutions appear, one of which extends from Mn_3Sb_2 to $MnSb$. Other end members of series of solid solutions whose compositions correspond to the law of multiple proportions are: $FeAl$, Al_3Mg_4 , $SbSn$, $PbTi_3$, $BiTi_2$, Ag_2Al , Ag_3Al and Ag_2Cd_3 .

Certain end members of the series of solid solutions are distinguished by melting point maxima as $TiCa$, $PbCa_2$ and Cu_4Ca . In the list of metallic compounds (Table 25) the non-singular crystalline varieties are noted by an asterisk.

In these cases it cannot be determined from the equilibrium diagram alone whether or not a compound occurs. The question whether a solid solution which is distinguished from the other end members of the series by a maximum on the melting curve is a compound cannot be determined merely on the basis of these maxima, for example, $ZnAu$, Tl_2Pb and $MgAg$.

These questions may be answered by the determination of the fusion

point lowering of the doubtful crystalline variety in a metal that forms no compounds with the components of the crystalline variety.

Von Wartenberg (*Zeitschr. f. Elektrochemie* 20, 449 (1914)) has been able to show by the determination of the vapor density of MgZn_2 at 1300° , that its vapor is completely dissociated, while according to Berry (*Proc. Roy. Soc., London, A*, 67 (1911)), zinc and MgZn_2 can be separated at 600° by distillation. Von Wartenberg has also shown that the compound Na_3Hg distills undecomposed at 400° .

The arc spectra of the crystalline varieties Cu_2Sb and Zn_3Cu_2 are the sum of the spectra of their components (*Zeitschr. f. anorg. Chem.* 92, 76 (1915)). On the other hand two lines appear in the spectrum of Mg_3Sb_2 which are lacking in the spectra of magnesium and antimony, and the Mg-line 383 is widened considerably. In general the arc spectrum of a metallic compound consists of the lines of its components, and deviations from this rule are not sufficient to prove the existence of metallic compounds with certainty at the high temperatures of the arc.

2. The Affinity Constants of Certain Metallic Compounds.

If a metal less noble than mercury is dissolved in mercury, the tension π changes linearly as the logarithm of the concentration C of the less noble metal (line 1, Fig. 146). If the same relation is investigated after having previously added to the mercury some other metal which is more positive than the one the concentration of which is being changed, the tension π changes with the log. C either along the practically straight line 2 that runs only slightly below the straight line 1, or along

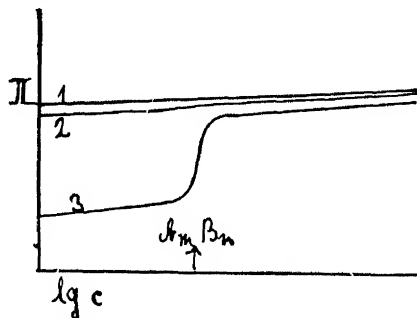


FIG. 146

the line 3 in which a very great change of tension takes place on exceeding a value of C , corresponding to the formula of a compound of the two metals, A_mB_n . The line 2 corresponds to such a metal pair whose compound dissolved in mercury has a vanishing small affinity constant; line 3 on the other hand corresponds to a metal pair with a very great affinity constant. (W. Jander and Tammann, *Zeitschr. f. anorg. Chem.* 124, 105 (1922).)

TABLE 27

	Li	Na	K	Rb	Cs	Ca	Ce
Na	o		Na ₂ K	—	—	—	—
K	o		—	—	—	—	—
Mg	o	o	o			Mg ₂ Ca ₃	Ce ₁ Mg; CeMg CeMg ₂ ; CeMg ₃
Zn	—	NaZn ₁₂	KZn ₁₂	—	—	CaZn ₁₀ ; CaZn ₄ Ca ₂ Zn; Ca ₂ Zn ₃ CaZn?	CeZn; CeZn ₂
Cd	LiCd LiCd ₂	NaCd ₅ NaCd ₂	KCd ₁₁ KCd ₇	—	—	Ca ₃ Cd ₂ ; CaCd ₂ CaCd	—
Hg	Hg ₂ Li Hg ₂ Li HgLi HgLi ₃ X	NaHg ₄ ; NaHg ₃ ; Na ₁₂ Hg ₃ ; NaHg; Na ₂ Hg ₂ ; Na ₂ Hg ₂ ; Na ₂ Hg	HgK; Hg ₂ K; Hg ₂ K ₂ ; Hg ₂ K ₂ ; Hg ₂ K	From 1.4-6.8 Rb investigated RbHg ₂	CsHg ₁₀ ; CsHg ₂ CsHg ₄ ; CsHg ₂ CsHg ₂ ; Cs ₂ Hg?	—	—
Cu	—	—	—	—	—	Cu ₂ Ca CuCa ₄ ?	CeCu; CeCu ₂ CeCu ₄ ; CeCu ₆
Au	—	Au ₂ Na	—	—	—	—	—
Ag	—	o	—	—	—	Ag ₂ Ca; Ag ₂ Ca Ag ₂ Ca; AgCa ₂ ; AgCa	—
Al	—	o	o	—	—	CaAl ₃	CeAl; CeAl ₂ Ce ₂ Al; Ce ₂ Al CeAl ₄
Tl	—	NaTl Na ₂ Tl? Na ₃ Tl?	KTl K ₂ Tl?	—	—	Tl ₃ Ca; Tl ₄ Ca ₃ TlCa	—
Sn	Li ₂ Sn ₅ Li ₃ Sn ₂ Li ₄ Sn	Na ₄ Sn Na ₂ Sn Na ₄ Sn ₂ NaSn NaSn ₂	KSn ₄ KSn ₂ KSn? K ₂ Sn? X	—	—	Up to 18 Ca investigated CaSn ₃	Ce ₂ Sn; Ce ₂ Sn ₂ CeSn ₂
Pb	—	Na ₄ Pb Na ₂ Pb NaPb Na ₂ Pb ₅	KPb ₄ ? KPb ₂ X K ₂ Pb?	—	—	Pb ₂ Ca; PbCa PbCa ₂	CePb ₂
Sb	—	Na ₂ Sb NaSb	—	—	—	Up to 9 Ca investigated X	—
Bi	—	Na ₂ Bi NaBi	KBi ₂ K ₂ Bi ₇ ? K ₂ Bi ₂ K ₂ Bi	—	—	Up to 10.1 Ca investigated X	BiCe ₂ ; Bi ₂ Ce ₄ BiCe; Bi ₂ Ce
Si	—	—	—	—	—	CaSi ₂	Up to 70 Ce investigated CeSi
S & Te	—	Na ₂ Te Na ₂ Te ₂ Na ₂ Te ₇	—	Rb ₂ S ₂ ; Rb ₂ S ₄ Rb ₂ S; Rb ₂ S ₆	Cs ₂ S ₂ ; Cs ₂ S ₂ Cs ₂ S ₄ ; Cs ₂ S ₅ Cs ₂ S ₆	—	—

TABLE 28

	P	As	S	Se	Te	Mn	P	As	S	Se	Te		P	As	S	Se	Te
As	—		fL 0-about 30 S KL 0-100 S	—	—		Investigated up to 33 P fL 0-33 P?	Investigated up to 57.3 As fL 5-40.5 and 46.3-57.3 As	—	—	—		Investigated up to 33 P fL 0-33 P?	Investigated up to 57.3 As fL 5-40.5 and 46.3-57.3 As	—	—	—
S	—			fL 80.2-90.2 Se at 160° and 15.8-58.8 Se at 75°	fL 2-98 Te KL 2-98 Te	Fe	Fe-Fe ₂ P fL 1-15? and 16-20.5 P KL below 800° 8.4-56 As	Investigated from 8.4 to 56 As fL below 800° 8.4-56 As	Fe-FeS fL 0-93 FeS KL 0-93 FeS	—	—		Fe-Fe ₂ P fL 1-15? and 16-20.5 P KL below 800° 8.4-56 As	Investigated from 8.4 to 56 As fL below 800° 8.4-56 As	—	—	—
Cu	Investigated up to 15 P fL 0-18 to 14.24? P	Investigated up to 44 As fL 0-44 As	Cu-Cu ₂ S fL 10-85 Cu ₂ S KL 0-94 Cu ₂ S	Cu-Cu ₂ Se fL 5-39? Se KL 0-39? Se	fL 4-48 Te KL 0-45 and 49.9-100 Te	Co	Investigated up to 21.2 P fL 0-21.2 P	Investigated up to 53.5 As KL > 1-53.5 As	Co-CoS fL below 790° 0-100 CoS	—	—		Investigated up to 21.2 P fL 0-21.2 P	Investigated up to 53.5 As KL > 1-53.5 As	—	—	—
Ag	—	Investigated up to 20 As fL 0-96 As	Ag-Ag ₂ S fL 12-100 Ag ₂ S KL 0-100 Ag ₂ S	Ag-Ag ₂ Se fL 7-26.9 Se KL 0-100 Ag ₂ Se	fL 0-100 Te KL 0-100 Te	Ni	Investigated up to 22.5 P fL 0-22.5 P at 20° Solid solutions from 17.35-18.1 at 1025°	Investigated up to 55.7 As fL 5.5-33.5 and 35.7-55.7 As	Ni-NiS fL 0.5-24.2 S and > 27 S-NiS? at 644° 0-100 NiS below 400°	—	—		Investigated up to 22.5 P fL 0-22.5 P at 20° Solid solutions from 17.35-18.1 at 1025°	Investigated up to 55.7 As fL 5.5-33.5 and 35.7-55.7 As	—	—	—
Au	—	Investigated up to 14 As fL 0-14 As	1	1	fL 0-100 Te KL 0-100 Te	Pt	—	Investigated up to 58.3 As fL 0-58.3 As	1	—	—		Investigated up to 58.3 As fL 0-58.3 As	Investigated up to 58.3 As fL 0-58.3 As	—	—	—
Zn	—	Investigated up to 14 As fL 0-14 As	—	—	—		Mo-Co Investigated up to 65 Mo fL 28-65 Mo	Ni-Mo Investigated up to 70 Mo fL 33-70 Mo	Fe-Mo Investigated up to 60 Mo fL KL?	Fe-V fL KL	Ni-V fL KL		Mo-Co Investigated up to 65 Mo fL 28-65 Mo	Ni-Mo Investigated up to 70 Mo fL 33-70 Mo	Fe-Mo Investigated up to 60 Mo fL KL?	Fe-V fL KL	Ni-V fL KL
Cd	—	Investigated up to 56.4 As fL 0-56.4 As	—	—	fL < 2.5-22 Te KL 0-22.5 and 29.4-100 Te		Cu-V fL 0-100 KL 0-100	Bi-I fL 2.2-49.8 I KL 0-100 I	I-Te fL 0-100 Te KL 0-100 Te	Br-I fL KL	Sn-I fL Sn-SnI ₂ and SnI ₂ -SnI ₄ KL 0-100 I		Cu-V fL 0-100 KL 0-100	Bi-I fL 2.2-49.8 I KL 0-100 I	I-Te fL 0-100 Te KL 0-100 Te	Br-I fL KL	Sn-I fL Sn-SnI ₂ and SnI ₂ -SnI ₄ KL 0-100 I
Tl	—	Investigated up to 50 As fL 0-50 As	Sn-SnS fL 4-19? S KL 0-20? S	fL 0-100 Se? KL 0-100 Se?	fL 0-100 Te KL 0-100 Te		Se-I fL 0-100 I KL 0-100 I	—	—	—	—		Se-I fL 0-100 I KL 0-100 I	—	—	—	—
Sn	—	Investigated up to 35 As fL 0-35 As	Pb-PbS fL 0-100 PbS KL 0-100 PbS	Pb-PbSe fL 0-100 PbSe KL 0-100 PbSe	fL 0-100 Te KL 0-100 Te		—	—	—	—	—		—	—	—	—	—
Pb	—	Investigated up to 35 As fL 0-35 As	—	—	fL 0-100 Te KL 0-100 Te		—	—	—	—	—		—	—	—	—	—
Sb	—	Investigated up to 13 As fL 0-13 As	Bi-Bi ₂ S ₃ fL 0-100 Bi ₂ S ₃	—	fL 0-100 Te KL 0-100 Te		—	—	—	—	—		—	—	—	—	—
Bi	—	Investigated up to 13 As fL 0-13 As	—	—	fL 0-100 Te KL 0-100 Te		—	—	—	—	—		—	—	—	—	—

1 The diagram not completed because of the volatility of one of the components.

1 The diagram not completed because of the volatility of one of the components.

TABLE 29

	P	As	S ¹	Se	Te	Mn	P	As	S	Se	Te
As	—	—	$\frac{AsS}{As_2S_3}$	—	—	—	Investigated up to 33 P $\frac{Mn_2P_2}{MnP}$	$\frac{Mn_2As}{MnAs}$	—	—	—
S	—	—	—	Se ₃ S?	0	—	$\frac{Fe-Fe_3P}{Fe_3P}$	Investigated from 8.4 to 56 As $\frac{Fe_3As}{Fe_3As_2}$ FeAs	Fe-FeS FeS	—	—
Cu	Investigated up to 15 P $\frac{Cu_3P}{Cu_3P}$	Investigated up to 44 As $\frac{Cu_2As}{Cu_2As_2}$	$\frac{Cu-Cu_2S}{Cu_2S}$	$\frac{Cu-Cu_2Se}{Cu_2Se}$	$\frac{Cu_2Te}{Cu_2Te}$	Fe	$\frac{Fe-Fe_3P}{Fe_3P}$	Investigated up to 53.5 As $\frac{Co_2As_2}{Co_2As_2}$ CoAs?	Co-CoS Co ₂ S Co ₂ S CoS	—	—
Ag	—	Ag ₂ As	$\frac{Ag-Ag_2S}{Ag_2S}$	$\frac{Ag-Ag_2Se}{Ag_2Se}$	$\frac{Ag_2Te}{Ag_2Te}$	Co	Investigated up to 21.2 P $\frac{Co_3P}{Co_3P}$	Investigated up to 55.7 As $\frac{Ni_2As_2}{Ni_2As_2}$ NiAs	Ni-NiS Ni ₂ S Ni ₂ S NiS	—	—
Au	—	1	1	1	AuTe ₃	—	Investigated up to 24.5 P $\frac{Ni_2P}{Ni_2P}$ Ni ₂ P	Investigated up to 28.3 As Pt ₂ As ₃	1	—	—
Zn	—	$\frac{Zn_2As_2}{Zn_2As_2}$	—	—	ZnTe	Ni	—	—	—	—	—
Cd	—	Investigated up to 56.4 As $\frac{Cd_2As}{Cd_2As_2}$	—	—	CdTe	Pt	—	—	—	—	—
Tl	—	—	—	—	$\frac{Tl_2Te_3}{Tl_2Te_3}$	—	—	—	—	—	—
Sn	—	Investigated up to 50 As $\frac{Sn_2As_2}{Sn_2As_2}$ SnAs	$\frac{Sn-SnS}{SnS}$	$\frac{SnSe}{Sn_2Se_2}$ $\frac{SnSe_2}{SnSe_2}$	$\frac{SnTe}{SnTe}$	—	Co-Mo Investigated up to 65 Mo $\frac{MoCo}{MoCo}$	Ni-Mo Investigated up to 76 Mo $\frac{NiMo}{NiMo}$	Fe-Mo Investigated up to 60 Mo X ²	Fe-V 0	V-Si VdSi ₃
Pb	—	Investigated up to 35 As 0	$\frac{Pb-PbS}{PbS}$	$\frac{Pb-PbSe}{PbSe}$	$\frac{PbTe}{PbTe}$	—	Bi-I BiI ₂ BiI ₃	I-Te $\frac{TeI}{TeI}$	Br-I BrI	$\frac{Sn-I}{SnI_2}$ $\frac{SnI_4}{SnI_4}$	Se-I 0
Sb	—	—	—	—	$\frac{Sb_2Te_3}{Sb_2Te_3}$	—	—	—	—	—	—
Bi	—	Investigated up to 13 As 0	$\frac{Bi-Bi_2S_3}{Bi_2S_3}$	—	$\frac{Bi_2Te_3}{Bi_2Te_3}$	—	—	—	—	—	—

¹ Diagram incomplete on account of the volatility of one of the components.² Compound forms very slowly.

TABLE 30

	Be	B	V	Be	B	V
Ag	f^- KL 0-93 Be			o		
Cu	Up to 25 Be investigated KL 1.5-12; 12.5-25 Be		fL 0-100 V KL 0-100 V	Cu ₂ Be CuBe ₂		o
Al	f^- KL 0-97 Be			o		
Fe	Up to 20 Be investigated KL 4-25 Be	Up to 8 B investigated KL 0.25-7.2 Be	f^- K-	FeBe ₂	Fe ₂ B ₂	o
Ni		Up to 22 B investigated KL 0-22 B	Up to 36 V investigated f^- K-		Ni ₃ Bi Ni ₃ B ₂ NiBi Ni ₂ B ₃	o
Si			Up to 60 V investigated KL 0-48 V			VS ₂
	Ce	W		Ce	W	
Fe	f^- KL 0-88 Fe	Up to 60 W investigated at 1420° KL 30W-? at 20° KL 20W-?		CeFe ₂ Ce ₂ Fe ₅	WFe ₂	

If the same tension of the binary and ternary amalgams correspond to the same concentration of the less noble metal, the concentration x of the less noble uncombined metal may easily be calculated. The equation of the mass law,

$$\frac{(A_mB_n)}{(A)^m(B)^n} = K \quad \text{becomes} \quad \frac{(A-x) + (A-x) \frac{n \cdot a_B}{m \cdot a_A}}{x^m \left(B - (A-x) \frac{n \cdot a_B}{n \cdot a_A} \right)^n} = K$$

In this equation a_A and a_B designate the atomic weights of the two dissolved metals. The affinity constant K is accordingly the only unknown.

It is found that the compounds of Zn with Cu or Ag dissolved in mercury are practically completely dissociated, while the compound ZnAu has the quite high affinity constant of 3.4×10^7 . With Cd-Cu and Cd-Ag amalgams very little evidence of compound formation is found while with Cd-Au it is lacking. With Pb-Ag amalgams no indications of Pb-Ag compounds are found, while the Pb-Au amalgams give weak indications of Pb-Au compounds. The compound CeSn₂ dissolved in mercury has an affinity constant of about 1.10^{40} , Ce₄Bi₃ about 1.10^{120} and Mg₂Sn about 1.1×10^{10} .

The affinity constants of metallic compounds are quite different.

Part of them dissolve in mercury with complete dissociation; others are not appreciably dissociated. To the first class belong compounds of metal pairs whose melting curve does not deviate appreciably from a line connecting the melting points of the two components. If, however, the melting curve has an outstanding maximum, the compound dissolved in mercury is not perceptibly dissociated.

3. The Ability of Elements to Form Compounds.

Mendelejew has divided the chemical elements into two small periods and four larger periods. The last two of these four large periods are made up in such a manner that analogous elements are missing in these two periods, analogs of the third large period missing in the fourth large period and the analogs of the fourth missing in the third large period. Only three elements are found in each of the four large periods which are evidently analogous to each other thus forming a natural group in the narrow sense.

One may expect from the elements of a natural group in the narrow sense that as chemical analogous bodies they would not form compounds. In fact the members of the following natural group in the narrow sense form no compounds with each other:

Cu	Zn	(Ge)	(As)
Ag	Cd	Sn	Sb
Au	Hg	Pb	Bi

However even with this cautious formulation, there is still an exception to this rule. Bromine and iodine, according to Meerum Terwoght (*Zeitschr. f. anorg. Chem.* 47, 202 (1905)), form the compound BrI which forms a continuous series of solid solutions with bromine as well as with iodine. The relation of these two elements is similar in this respect to that of magnesium to cadmium. Also tin and lead seem to form a compound $\text{Pb}_4\text{Sn}_3(?)$.

Since the members of both small primary periods frequently form compounds with each other, as carbon and silicon, oxygen and sulphur, fluorine and chlorine, and since the elements of both small primary periods not unfrequently form compounds with the elements of their natural groups in the narrow sense, as sodium with potassium, magnesium with calcium, oxygen with selenium and tellurium, and chlorine with bromine and iodine, the former rule is not general. It is obvious that the elements of a natural group in the narrow sense, although not always are generally of so similar a structure that they form no compounds with each other. Similarly the members of a homologous series form no compounds.

For the chemical relation of metals to each other we may formulate the following rule:

A given element forms either a compound with all elements of a natural group in the narrow sense or with none of the members of the group.

With oxygen, sulphur and halogen-compounds we find numerous confirmations of this rule; it is true that compounds are noted here with all natural groups up to those of the inert gases. As a rare exception to this would be the case where oxygen forms no compound with fluorine although oxygen forms compounds with the other halogens.

This rule is convincingly illustrated by the relation of metals of the copper group to other metals. Table 25 contains the formulæ of compounds. If the two metals form no compound in a temperature interval from about 200° above its melting point to room temperature it is indicated by the symbol o.

For the binary combinations of the elements of the copper group with 17 other elements, two exceptions are found to this rule; gold forms two compounds with lead, while lead forms no compounds with copper and silver in the investigated temperature interval; silicon forms compounds with copper while it does not combine with silver. These results would be still more favorable to the rule if the relation of the metalloids to copper, silver and gold were considered.

We will obtain just as favorable results with the investigation of the ability of the elements of the zinc group to form compounds. There are three exceptions in the binary combinations with 15 foreign metals including the sodium compounds. These exceptions are aluminum, tellurium and tin. Zinc forms a compound with aluminum while cadmium on the other hand does not; while zinc and cadmium form no compounds with tellurium, tellurium forms a compound with mercury according to Kurnakow, and while tin forms no compound with zinc, both mercury and cadmium give a compound with tin.

In the group containing nickel, palladium and platinum there is one exception found in 19 binary combinations. Since platinum and palladium give compounds with lead, then nickel should also give a compound with lead, but upon heating the two metals a little above the melting point of nickel, a compound cannot be found.

With these natural groups in the narrow sense there is a complete analogy of the group members with respect to foreign elements; these groups act accordingly toward other elements as members of a homologous series of carbon compounds, which either all react with a foreign body or else none do.

The members of those groups, however, in which a transition of metalloids to metals takes place, as in the groups of arsenic, antimony and bismuth or germanium, tin and lead, do not form homologous series as regards their ability to combine. We find from the tables that tin and lead act similarly only in seven combinations, that they differ in seven other combinations and that if tin forms a compound lead does not. Only in the case with tellurium is the reverse true. Even the existence of the compound $PbTl_2$ is not proven. The curve of the beginning of crystallization of the series of Pb-Tl solid solutions has a maximum at this composition.

The relation of antimony and bismuth to other metals differs still

more. Except for the sodium compounds, the relation of the two elements with 16 binary combinations is only similar in six cases; ordinarily bismuth forms no compound when antimony does.

The elements antimony and bismuth, as well as tin and lead, stand much further apart than the elements of the copper or zinc groups.

The position of the metals of the rare earths in the periodic system has been discussed to quite an extent. The relation of the rare earth metals to other metals is well determined. According to R. Vogel (*Zeitschr. f. anorg. Chem.* 75, 41 (1912); 84, 323 (1913) and 102, 177 (1917)), these metals form a natural group. The only thoroughly investigated metal of this group, cerium, forms compounds with aluminum, tin, lead and bismuth with high heats of combination and high melting points.

4. The Valence of Metals in Their Compounds.

The conception of valency has been demonstrated quite largely in two large groups of chemical compounds, the carbon compounds and salts. On the other hand we know that with the binary compounds of elements whose properties approach those of the metals, as for example the sulphides and arsenides, the formulæ do not correspond to saline valencies. Even in the oxides, which stand in closer relation to the salts, only a portion of the formulæ correspond to the saline valencies. Only in the binary compounds of the halogens with the metals, except some high iodine compounds, will the saline valence determine the formula; these compounds are, however, typical salts.

In the compounds of metals, formulæ corresponding to saline valencies of the metals appear relatively seldom. However, since the valence can change only within narrow limits, the appearance of saline valencies can frequently be observed in the formulæ of the metallic compounds. Individual properties of the elements appear more distinctly in the binary metallic compounds than in salts, in which the chemical character of an element frequently plays so unessential a rôle, that metals, as in alums, which differ from each other in other essentials are able to replace each other.

Of about 150 compounds which Table 25 contains, only the formulæ of about 35 compounds really agree with the saline valence of the metals. These formulæ are underlined. In the compounds of copper it occurs 5 times, in the compounds of tellurium 4 times, in those of silver 3 times, in those of bismuth twice and only once in those of gold, 7 times in the compounds of magnesium and 14 times in those of antimony. Antimony is the one metal whose compounds agree mostly with the saline valence and of the elements mentioned, antimony stands closest to the characteristic metalloids.

However, the individual behavior of the metals in their compounds extends further. The formulæ of the compounds of the metals of a natural group in the narrow sense with a foreign element, notwith-

standing the far-reaching chemical analogy of the members of a natural group, are not always analogous.

Add to this that among intermetallic compounds, such extraordinary formulæ occur as NaZn_{12} , KZn_{12} , NaCd_5 , NaHg_4 , FeZn_7 , NiZn_3 , NiCd_4 and AuSb_2 , which are incontrovertible contradictions to the saline valence. We may accordingly conclude that the formulæ of binary compounds, which are not salts or salt-like are not determined by the saline valency.

5. The Isomorphism of Elements.

Two substances, which form a continuous series of solid solutions with each other are isomorphous. Their crystal form and space lattice are of the same kind. The reverse of this rule does not, however, hold. If the space lattice of a metal is known through its Röntgenogram, then all metals which form a continuous series of solid solutions with this metal have lattices of the same kind, only the distances of the atoms from one another will differ. According to the postulate of Mitscherlich only substances of analogous chemical composition form continuous series of solid solutions with each other.

If an arrangement of the periodic system is made in which the chemical analogies of the elements are expressed by the distances between them, accordingly chemically analogous elements being closer together than those chemically different, the isomorphous elements will be found in the middle of this arrangement.

Such an arrangement of the periodic system is found in Table 31. (The temperature of the melting points is indicated below the symbol of the element.) If we put down the two short and five long periods under one another, so that the elements of a natural group form a vertical series, the intervals between the most dissimilar elements as the alkalis and halogens are great, while those of the closely related elements as Co and Ni are very small. The boundary between metals and metalloids at which the chemical properties change considerably is indicated in the table by a heavy broken line. Continuous series of solid solutions form in the following pairs of elements: Cu-Au, Cu-Mn, Cu-Ni, Cu-Pd, Cu-Pt, Ag-Au, Ag-Pd, Au-Pt, Mg-Cd, Pb-In, Sb-Bi, Mn-Fe, Mn-Co, Mn-Ni, Fe-Co, Fe-Ni, Fe-Pt, Co-Ni, Co-Cr, Ni-Pd, Li-Cd, Fe-V, Br-I.

These elements occur in Table 31 either in the center or in a natural group in the narrow sense, accordingly between chemically similar elements, hence one may assume an analogous structure of the middle elements of the system.

A rule regarding the position of the solubility gap. On crystallization from binary melts more of the element with the lower melting point dissolves in the crystals of the element with the higher melting point, than vice versa. For this rule it is immaterial whether the concentration of the solid solution is measured by atomic per cent. or per cent. by weight.

TABLE 31

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
H —259	He below —268	Li 186	Be >1800	B 1278	C Not fusi- ble											N —210	O —218	F —223
	Ne —253	Na 98	Mg 650	Al 658	Si 1420											P 44 and 630	S 119	Cl —102
	Ar —189	K 62	Ca 805	Sc 1000 to 1400?	Ti 2200?	V 1800	Cr 1520	Mn 1207	Fe 1530	Co 1480	Ni 1450	Cu 1083	Zn 419	Ga 30	Ge 958	As 814	Se 220	Br —7
	Kr —169	Rb 38	Sr Red heat	Y 1490	Zr 1700?	Nb 1700	Mo 2430		Ru 2480	Rh 1970	Pd 1557	Ag 961	Cd 321	In 155	Sn 232	Sb 630	Te 450	I 113
	X —140	Cs 26	Ba 850	La 810	Ce 700	Nd 840?	Pr 940											
				Yb		Ta 2830	W 3060		Os 2740	Ir 2400	Pt 1764	Au 1063	Hg —39	Tl 301	Pb 327	Bi 270		
			Ra 600 to 1200?		Th 1800		U 1860											

In the following summary is indicated below the symbol of a metal, the per cent. of the other metal soluble in it.

(a) The two metals form no compounds

Ag-Cu, 4.5 5	Cu-Fe, 2.5 9 at 1100°	Cu-Co, 4 10	Ag-Tl, 10 0	Ag-Bi, 5 0	Ag-Ni, 0 4	Ag-Si, 0 10	Au-Tl, <4 0
Au-Bi, 4 0	Cd-Pb, 0 6	Hg-Pb, 0 35	Tl-Mn, 0 2	Tl-Ni, 0 2	Sn-Cr, 0 5	Pb-Ni, 0 4	Sb-Si, 0.3 1.1
Ag-Na 2 0							

Exceptions

Au-Fe, 20 18 at 20°	Au-Co, 6 3.5	Cd-Hg, 34.8 62.7 at 188°	Zn-Sn, 0 1	Tl-In, 30 63	Zn-Bi, 0 2	Ni-Cr, 57 42	Bi-Si, 0.8 0
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(b) The two metals form compounds

Cu-Al, 9 4	Cu-Sb, 1.5 0 at 20°	Cu-Zn, 36 3 at 20°	Cu-Co, 4 10	Ag-Mg, 8 0	Ag-Zn, 21.7 10	Ag-Cd, 36 6	Cu-Sn, 13 0 at 20°
Ag-Al, 5 0	Ag-Sn, 19 0	Ag-Sb, 15 0	Au-Mg, 2.9 0	Au-Cd, 18 0	Au-Sn, 4 0	Mg-Tl, 46.5 0	Zn-Al, 1 38
Zn-Fe, 0.7 20	Zn-Ni, 0 46	Hg-Sn, 0 22	Al-Mn, 0 about 30	Fe-Al, 34 0	Al-Co, 0 9.5	Al-Ni, 0 15	Tl-Pb, 6 77
Pb-Sn, 18 0.37 at 181°	Sn-Sb, 8 10	Sn-Mn, 0 10	Sn-Fe, 0 19	Sn-Ni, 0 15	Pb-Bi, 33.5 13 at 125°	Pb-Pd, 0 23	Sb-Fe, 0 5
Sb-Co, 0 12.5	Sb-Ni, 0 7.5	Sb-Pd, 0 15 at 20°	Sb-Cr, 0 10	Bi-Ni, 0 0.5	Fe-Si, 20 0 at 1240°	Cd-Ca, 0 13	Na-Pb, 0 0.5
Te-S, 2 2							
Tl-Bi, 7 0							
Sn-Co, 0 2.5							
Ni-Si, 67.6 24							

Exceptions

Cu-Si, 4.5 0	Ag-Mn, 20 0	Au-Zn, 12.5 21	Cd-Sn(?), 0 7.5	Sn-Bi, 6 0	Mn-Si, 10 0	Si-Co, 9 7.5	Cu-Ca, 0 30 at 20°
S-Se, 80.2 9.8 at 160°							

It will be noted that exceptions to this rule occur only when the melting points of the two metals differ but slightly.

F. The Equilibrium Diagrams of Special Binary Systems

In the preceding chapter the relations of metals to one another as they are described in an exact and comprehensive manner by the equilibrium diagrams of the binary mixtures, have been considered from a general viewpoint. In conclusion a summary is given of the most important characteristics of the relations of two metals to each other.

For many cases, which require a comprehensive knowledge of the equilibrium diagram this information is not sufficient. In what follows we have accordingly collected the equilibrium diagrams of several technically important systems with special data concerning the behavior of the alloys given. The alloys considered are principally those of Iron and Copper.

It will be readily understood that even when an equilibrium diagram has been studied rather exhaustively, special questions will still arise which can only be solved by further investigation. This is especially true of the Iron-Carbon diagram.

It must not, however, be assumed that this is the only diagram which has offered difficulties. There are unanswered questions concerning many other diagrams.

It is quite understandable that a substance so important industrially as Carbon steel should present so many questions. The more frequently a thing is observed the more new peculiarities are discovered, and such is the case with steel.

Science seeks to grasp the general and therefore may not pursue many of the secondary phenomena so long as it attains its principal objective, while in practice in order to attain a definite objective particular control must be had over certain disturbing or useful secondary phenomena.

It would, however, be absurd not to use these things in practice because the scientific bases are still incomplete. It is generally recognized today that the scientific bases of practical processes are of the greatest importance and that in return science derives considerable benefit from industrial practice.

1. Iron—Carbon.

Because of the great economic importance of the Iron-Carbon alloys, it would be expected that the details of their formation would be definitely established. This is, however, unfortunately not the case in every respect.

To Osmond (*Contributions à l'étude des Alliages*, Paris (1901), 277) and Roberts-Austen (*Proc. Inst. Mech., Eng.* (1897 and 1899)) we owe the establishment of the fundamental principles. To Le

Chatelier (*Rev. gén. des Sciences* (1897), 11) the explanation of the processes depending on the transformations in the Iron-Carbon alloys. Roozeboom (*Zeitschr. f. phys. Chem.* 34, 437 (1900)) undertook to combine all the known facts into a diagram; he did not, however, differentiate between the stable and metastable crystalline varieties which appear in the Carbon steels. The errors occurring in this were corrected by the investigations of Heyn (*Zeitschr. f. Elektrochem.* 10, 437 (1904)) and Charpy (*Bull. Soc. d'Encourag. de l'Industrie* (1902), 399) so that the fundamentals of the genesis of the Iron-Carbon alloys up to 6 per cent. Carbon appear to be established.

For Iron-Carbon alloys with more than 6 per cent. Carbon the opinions according to the latest investigations of Ruff (*Metallurgie* 8, 456 (1911)), Wittorff (*Zeitschr. f. anorg. Chem.* 79, 1 (1912)) and Hanemann (*Zeitschr. f. anorg. Chem.* 84, 1 (1913)) differ considerably. Since cast irons with more than 4 per cent. Carbon find little use in industry we will not consider them here.

The solubility of graphite in liquid iron up to 2500° was investigated by R. Ruer (*Zeitschr. f. anorg. u. allg. Chem.* 113 (1920)). The method depends on the fact, that upon rapid cooling the graphite crystals formed in the liquid iron do not appear on the surface of the liquid iron, although the difference in density between it and the liquid in which it is formed is quite considerable. If, then, a liquid iron is saturated with graphite at a definite temperature and the melt cooled quickly, the total carbon content of the solidifying regulus gives the amount of dissolved carbon at the concerned temperature, the solubility of the graphite. In Fig. 147, the curve C'D' is the solubility curve of the graphite. With rising temperature the viscosity of the liquid iron with graphite increases perceptibly from 1880° , which shows that the amount of the liquid solution in the mold decreases with increasing temperature. At 2500° the melt becomes pasty, the impression of a stirring rod of graphite remains in the pasty melt even after cooling.

(a) The crystallization of iron-carbon melts. From melts rich in carbon two substances can crystallize as primary constituents, graphite and Fe_3C . From the same melt we can obtain either a white cast iron or a gray cast iron. By a rapid cooling a white cast iron is obtained without graphite and with the primary formation of Fe_3C . By slow cooling a gray cast iron is obtained with a primary formation of graphite. From this we conclude that the number of crystallization centers of Fe_3C increases very much faster with the degree of supercooling than does that of graphite.

Not only the rate of cooling but also the content of impurities exert a great influence upon the ratio of the numbers of crystallization-centers of Fe_3C and graphite. With increasing manganese content the number of Fe_3C centers increases and the nucleus number of graphite decreases while an increasing silicon content exerts an opposite influence.

It has been shown further that if a graphite-free iron containing Fe_3C is given a long period of annealing at a temperature of 1000° , graphite will form at the expense of the Fe_3C . Hence Fe_3C is less stable than a mixture of Fe and graphite.

From a melt with less than 4.2 per cent. carbon cooled at an average rate, solid solutions rich in iron will crystallize carbon content of which can amount to 2 per cent. at the most.

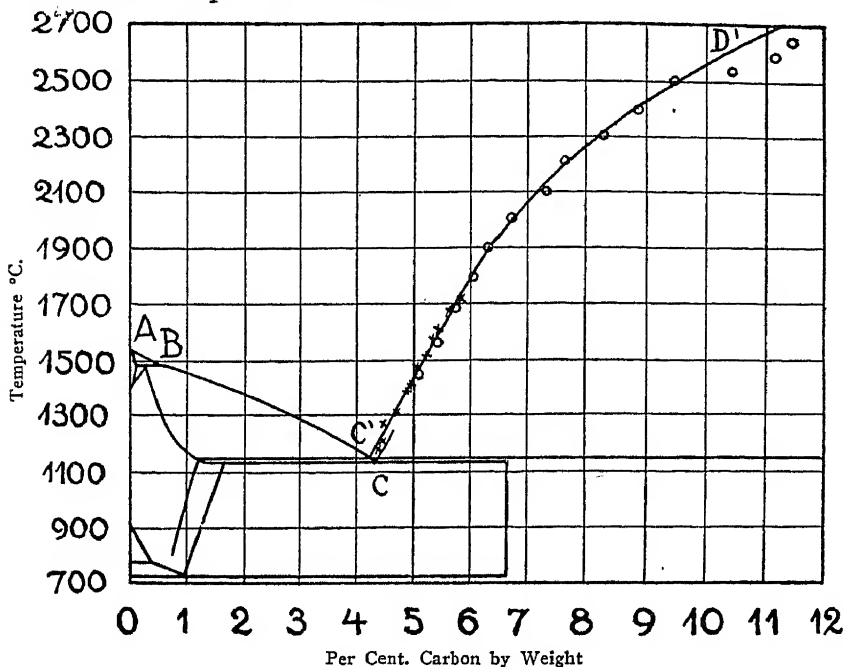


FIG. 147

Investigations have shown that in other low melting substances, supersaturated solid solutions are not infrequently formed by rapid cooling (p. 26). On the other hand unsaturated solid solutions can also deposit upon quick cooling. In the supersaturated as well as in the unsaturated solid solutions, the distribution of the two atomic varieties is not the normal one which corresponds to the stable condition. This only takes place with time, and much quicker at higher temperature.

From these experiments the diagram, Fig. 148, is derived. It does not indicate the temperature accurately because the positions of the points b , e_1 , e_2 and b_1 are not accurately determined and secondly it was desired for clearness to separate the points b and b_1 whose temperatures probably differ by only 15° . The curve g_1 is that of

the beginning of the crystallization of the stable unsupersaturated solid solutions, g_2 is its accompanying curve for the completion of crystallization. The point of intersection of the curve g_1 with the solubility curve of graphite b corresponds to the eutectic point of the stable equilibrium between the melt b , the graphite and the saturated solid solution a . The points of these lines are found either by cooling the melt very slowly or more easily by heating the material, which has been heated to nearly 1200° for a long time to produce a stable equilibrium.

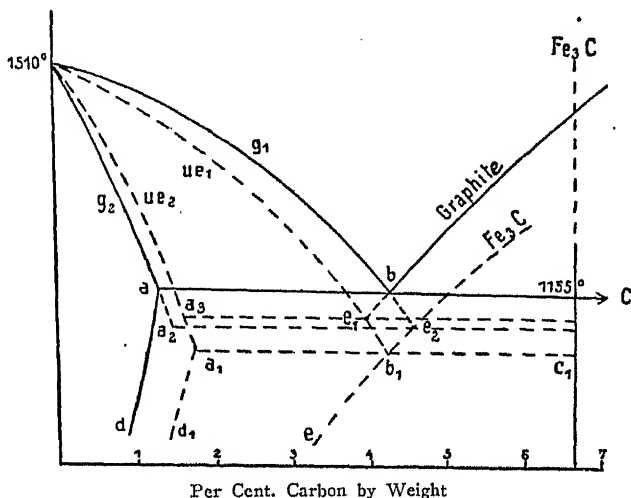


FIG. 148

By the customary rate of cooling, metastable supersaturated solid solutions will crystallize from the melt up to about 4 per cent. carbon. Their curves of the beginning and completion of crystallization are ue_1 and ue_2 . On account of the change of carbon content in the primary separation it is necessary to consider a different curve of the beginning of crystallization for every rate of cooling. The temperature of these curves decreases with increasing cooling rate. The corresponding curves for the completion of crystallization will accordingly be displaced toward higher carbon concentration and also towards higher temperatures. The Fe₃C on the one hand, and the supersaturated solid solution a_1 on the other are not in stable equilibrium with the melt b_1 . If no graphite crystals formed, the crystallization of melts with more than 2 per cent. would end through the division of the melt b_1 into a_1 and Fe₃C, whose composition corresponds to the point c_1 . In reality, the crystallization of melts with more than 3 per cent. carbon will proceed to completion according to the conditions of spontaneous crystallization, the cooling rate, the manganese and silicon content, due

to the formation of somewhat different solid solutions and eutectics at different points of the same melt at different temperatures.

The four curves of the beginning of crystallization g_1 , ue_1 , and the solubility curves of graphite and Fe_3C intersect at the four points b , b_1 , e_1 and e_2 . The point b lies at 1150° , the point b_1 at 1140° . According to G. Charpy (*Compt. rend.* 141, 948 (1905)) their difference amounts to about 15° . How the crystallization proceeds to

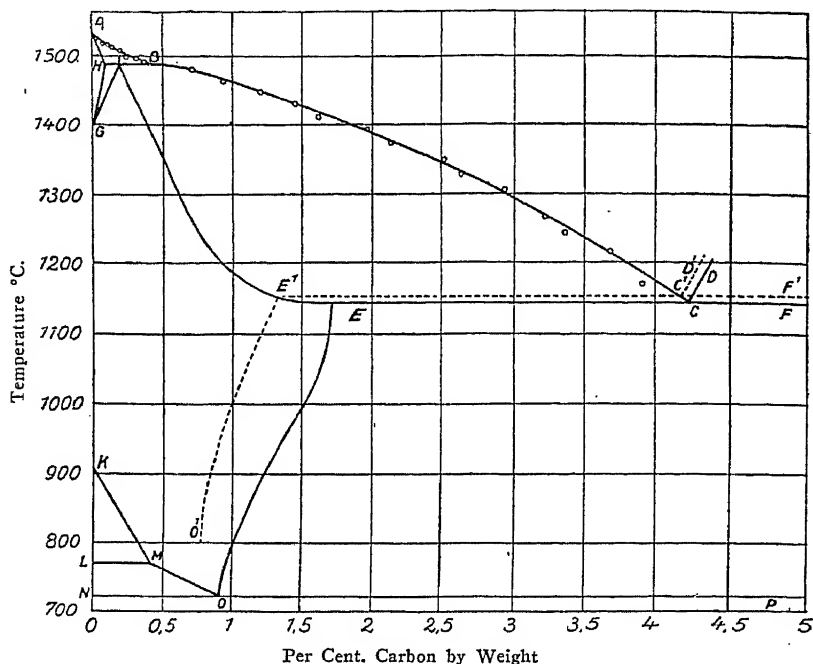


FIG. 149

completion depends entirely upon which two of the possible crystalline varieties, graphite and a or a_3 on the one hand, Fe_3C and a_1 or a_2 on the other, will form simultaneously from the concerned portion of the melt. Corresponding to the two kinds of crystals the temperatures at their contacts with the melt are those of the intersections of the two saturation curves.

If in the entire melt more than one crystalline variety forms at the beginning of crystallization and more than two crystalline varieties form at the completion of crystallization, the temperature during crystallization, even if the melt is stirred, must be different locally corresponding to the difference in local equilibria. The entire process of crystallization from a melt, from which graphite and Fe_3C separate

simultaneously is indefinite but it may be divided into several definite simultaneous and consecutive processes.

Fig. 149 is the actual diagram corresponding to Fig. 148. The broken line $E'F'$ corresponds to the graphite-eutectic line aC of Fig. 148 and the line EF , the cementite-eutectic.

Upon rapid cooling of an iron with 3 per cent. carbon by casting in an iron mold, the crystallized mass at the point of the greatest cooling rate consists only of Fe_3C and the solid solution a_1 . Owing to the great supercooling taking place in the melt, an Fe-rich solid solution does not separate out first, but as may be concluded from the structure, the long needles of Fe_3C crystallize first when the temperature is lowered below the extension eb_1 of the solubility curve of Fe_3C . Finally the crystallization is completed with the formation of a solid solution. With a medium cooling rate the average cast iron contains graphite and a_3 besides Fe_3C and a_1 . Here, portions of the eutectic structure first form in the vicinity of the graphite-spherulites. By cooling still slower, chiefly graphite and a_3 form with only small amounts of Fe_3C and its accompanying solid solutions a_2 or a_1 .

For the coördinates of the line ad , Fig. 148 ($O'E'$, Fig. 149) of the stable systems, the following values have been determined by Ruer and Iljin (*Metallurgie* 8, 97 (1911)).

1120°	1.25% C.
1000°	0.99% C.
800°	0.75% C.

Graphite can be easily obtained from supersaturated solid solutions in the form of temper carbon by annealing under 800° which is again absorbed by heating to a still higher temperature.

(b) The transformations in carbon steels with 0.2 per cent. carbon upon slow cooling. After the completion of the crystallization at normal cooling rates, the alloys from 0 up to about 2 per cent. carbon consist of solid solutions, whose average composition agrees with that of their melts. According to the investigations of Gutowsky (*Metallurgie* 6, 731 (1909)), the solid solution a_1 contains 1.7 per cent. carbon. In the alloys of 2.0 to 4.2 per cent. carbon, the saturated solid solution a_1 is surrounded by a eutectic, consisting of Fe_3C and a_1 , yet here, especially in the carbon-rich alloys, graphite formation always occurs and therefore crystallizes with less than 1.7 per cent. carbon, the solid solutions a_3 and a are also present. Finally in the alloys with 4.2 up to 6.8 per cent. carbon, if no formation of graphite occurred, the primary crystals of Fe_3C would be surrounded by the eutectic $a_1 + Fe_3C$. Still in these alloys a considerable amount of graphite forms at first.

In what follows we will deal exclusively with the alloys from 0 to 2.0 per cent., which have been rather quickly cooled and therefore contain no graphite.

Practically C-free iron shows after its complete crystallization, three

arrests on its cooling and heating curves, 1401° , 906° and 769° . Accordingly four thermally different crystalline varieties of iron δ -, γ -, β - and α -iron must be differentiated. Crystallographically according to Osmond (*Contribution à l'étude des alliages*, Paris (1901), 277) β - and α -iron cannot be distinguished; both crystallizing in cubes. In γ -iron octahedral faces also occur.

The transformation point of δ - into γ -iron at 1401° has been observed by Gontermann (*Zeitschr. f. anorg. Chem.* 59, 378 (1908)). Ruer and Klesper (*Ferrum* (1914), p. 260) have worked out the portion of the diagram in which the transformation of δ - into γ -iron occurs. Fig. 149 is a copy of the diagram plotted by Ruer and Goerens (*Ferrum* (1916-17), p. 161). The temperature of the transformation of δ - into γ -iron increases with increasing carbon content. At 1486° the melt with 0.38 per cent. carbon is in equilibrium with the γ -solid solution with 0.18 per cent. carbon and the δ -solid solution with 0.07 per cent. carbon. In steels with more than 0.4 per cent. carbon the transformation of δ - into γ -iron does not occur because the γ -solid solution is precipitated from their melts.

If the temperature of the γ -iron falls below 906° , about 2.9 calories are liberated per gram and the volume diminishes about 0.001 cm.³ per gram of iron. If the transformation occurs after supercooling, the temperature increases a little during the cooling and then retards before falling; the glowing piece of iron brightens somewhat (recalescence). By this reaction β -iron is formed from γ -iron.

At 769° the β -iron transforms into the α -iron, stable at lower temperatures. A perceptible change of volume does not accompany this transformation. Also the heat liberated is considerably smaller than in the transformation of γ - into β -iron; it is about 1 calorie per gram. A new property occurs, however, on this transformation, namely, a high magnetic susceptibility, ferromagnetism, which is especially characteristic of α -iron but is almost completely lacking in β -iron and is entirely missing in γ -iron. The loss and recurrence of ferromagnetic properties are extremely characteristic of the reversible transformation of β - into α -iron.

The influence of the carbon content upon the equilibrium temperature of β - and α -iron with the solid solution of γ -iron is observed in Fig. 149. This representation is based on the assumption that pure β - or α -iron separate from the γ -solid solution.

The field of the γ -solid solution is bounded at lower temperatures by the lines KM and MO , in which γ -solid solutions are in equilibrium with β - or α -iron. We will now follow the transformation of the γ -solid solution on slow cooling, because it is assumed that meta-stable crystalline varieties are not formed by sufficiently slow cooling.

If a γ -solid solution with a little less than 0.4 per cent. carbon is cooled, upon reaching the line KM , β -centers will form at points in the solid solution, which grow and hence force out the carbon in the γ -iron, as carbon is only slightly soluble in the β -iron. When the

temperature reaches the point M , the β -iron is transformed into the magnetic α -iron, as indicated by the horizontal $L M$.

The γ -iron is now so concentrated in carbon that nuclei of α -iron can form in it. Since the progress of nuclei formation is not directly



FIG. 150

Iron with 0.14%. Etched with tincture of iodine. The crystallites of Fe are attacked unequally by the etching medium. The dark flakes are pearlite which is present in all of the crystallites in equal amounts. $\times 1000$.

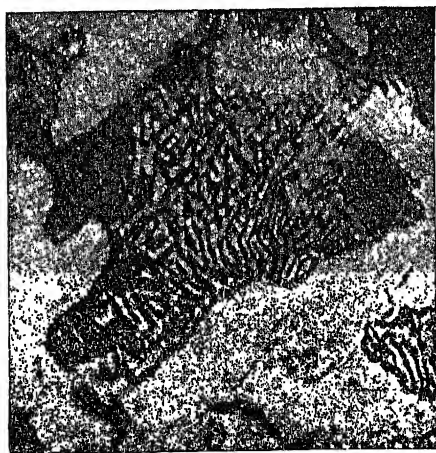


FIG. 151

Iron with 0.40% C. The light parts are ferrite (Fe), the dark pearlite. $\times 1000$.



FIG. 152

Iron with 0.9% C. Consisting entirely of pearlite alternating hard lamellae of Fe_3C and soft of Fe. $\times 1000$.

influenced, however, by the new limitations of equilibrium, it is very probable that by further increase of carbon content in the γ -solid solution, nuclei of α -iron will not form but rather nuclei of β -iron, which, however, soon become transformed into α -iron.

Finally when the carbon content of the remainder of the γ -solid solution is increased up to the point *o* at 0.9 per cent. carbon, the solid solution is not only saturated in respect to α -iron but also with respect to a second substance, whose solubility curve is the line proceeding from *O* in the direction towards *E*. By further abstraction of heat the solid solution *O* dissociates into α -iron and this substance. By the splitting up of this doubly saturated solid solution *O*, the resulting constituent is pearlite, which appears on a polished surface etched with

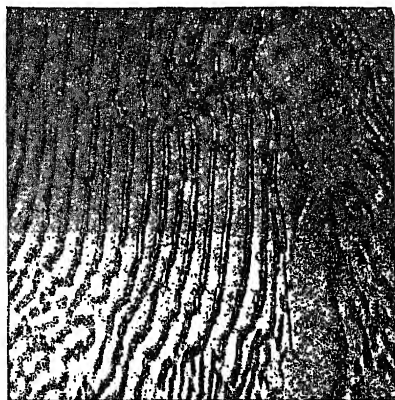


FIG. 153

Iron with 1.75% C. Mostly pearlite, with a band of cementite at the right.
 $\times 1000$.

alcoholic solution of picric acid as lamella of a white substance, α -iron, and a hard substance of pearlite-cementite. This interpretation of the transformation corresponds also to the appearance and disappearance of ferromagnetic magnetizability. The temperatures of the loss of magnetizability on heating and its recurrence on cooling, lie according to M. Levin on the line *L M O P*, which agrees completely with the above description of the reactions taking place on slow changes in temperature.

Corresponding to these changes caused by the described transformations, the steels with 0 to 0.9 per cent. carbon from ordinary temperatures up to 700° , consists of α iron-crystals (Ferrite) surrounded by pearlite, whose amount increases with increasing carbon content (Figs. 150 and 151) up to the steels with 0.9 per cent. carbon consisting entirely of pearlite (Fig. 152). In the steels with 0.9 to 2.0 per cent. carbon, primary cementite (Fe_3C) formed from the γ -solid solu-

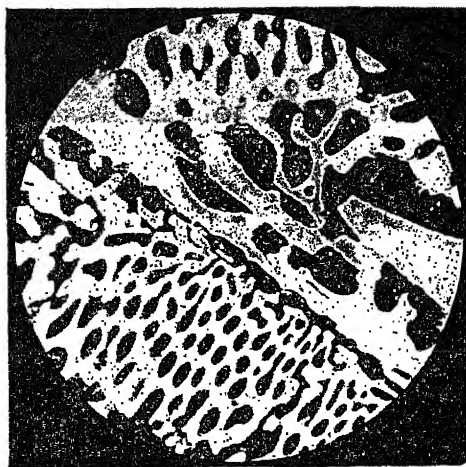


FIG. 154

White cast iron with about 3% C. Etched with picric acid. The light parts are cementite, the dark pearlite. The large dark parts consist of a primary formation and are surrounded by cementite and a eutectic consisting of cementite and pearlite. $\times 500$. From Guillet. *Trempe, Recuit, Revenue* Plate 4, Fig. 14.

tion is surrounded by pearlite, whose amount diminishes with increasing carbon content (Fig. 153).

In the cast irons with 2 to 4.2 per cent. carbon, primary γ -solid solutions formed from the melt are dissociated into cementite and



FIG. 155

Iron with 4.6% C. Primary cementite. $\times 200$. From Gutowsky, *Metallurgie*, 6, 737, Fig. 267 (1909).

pearlite and are surrounded by a eutectic of cementite and the existing γ -solid solutions, that have formed from the melt. The γ -solid solutions of this eutectic are in return dissociated into cementite and pearlite (Fig. 154). Finally in the rapidly cooled white cast iron with more than 4.2 per cent. carbon, primary cementite is formed from the melt, surrounded by the eutectic of the original γ -solid solution and cementite (Fig. 155), and in a slowly cooled gray cast iron, a portion of the primary cementite formed is replaced by graphite (Fig. 156).

Is the pearlite-cementite identical with the Fe_3C formed in carbon-iron melts? M. Levin and A. Meuthen (*Ferrum* 10 (1912)) have



FIG. 156

Gray cast iron. Etched with picric acid. Graphite (black). Pearlite, cementite (white). $\times 200$. Guillet, l. c. photo. 11.

determined that the heat content of steel with 0 to 6.6 per cent. carbon is not a linear function of the carbon content between 700° and 660° but is represented by two straight lines, whose intersecting point lies as 0.95 per cent. carbon. If the pearlite-cementite is identical with the cementite (Fe_3C) formed from the melt, the heat content of the steel between the composition of iron (Fe) and cementite (Fe_3C) must be a linear function of the carbon content. Since, however, that is not the case and the difference of the heat content found and that calculated from the linear relation is greatest in the composition of the pearlite, then the pearlite-cementite must possess a little greater heat content than the cementite formed from the melt.

K. Honda and Takagi (*Science Reports, Tohoku Univ.*, 4, 161

(1915)) found a transformation point for cementite as 210° . At this temperature the cementite loses its ferromagnetism upon heating, which returns at this temperature upon cooling. Since the change of magnetism at 210° is a linear function of the carbon content of the iron, then this change for same amounts of the three cementite varieties is the same, namely the pearlite and that formed from the solid solution and the melt. These cementite varieties have the same space lattice and the variation in the heat content of the pearlite and the cementite forming from the melt are a result of its different grain size. The fine pearlitic cementite, which has a much larger surface



FIG. 157

Austenite 2% C, 2.2% Mn. Quenched from 1050° . $\times 400$. Maurer.

than that arising from the melt, has in consequence of its fineness a larger heat content.

Even the relation of the electrical resistance and of the coercive force to the carbon content is represented by two straight lines, which intersect at the carbon content of the pearlite. This fact can be attributed to different distributions of the cementite in hypo- and hyper-pearlitic steels.

The loss of the magnetization of cementite according to K. Ewig (*Stahl u. Eisen* 42, 772 (1922)) is accompanied by a change in volume which can influence unfavorably the tensile properties of material rich in cementite.

(c) The effect of rapid cooling. In the interpretation of the reaction upon quenching of γ -solid solutions, considerable emphasis is placed on the change of magnetic properties. We have seen that the

magnetizability changes discontinuously with changes of state of aggregation, and that in other respects it does not depend very greatly on the temperature and frequently is independent of the temperature (p. 51).

β -iron, γ -iron and the solid solutions of the γ -iron are paramagnetic, while α -iron is ferromagnetic. If upon quenching γ -iron or its solid solution a non-ferromagnetic product is obtained it can be assumed to be γ -iron or γ -solid solution. In fact small amounts of ferromagnetic iron can always be detected following quenching of γ -iron. Yet if the γ -iron contains over 1 per cent. carbon, it will be only slightly ferromagnetic after quenching and with a content of 2 per cent. carbon and 2 per cent. manganese, Maurer (*Metallurgie* 6, 33

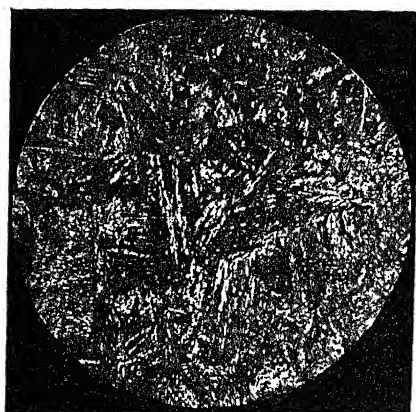


FIG. 158

Martensite. $\times 300$. Oberhofer.

(1909)) obtained upon quenching, a paramagnetic body whose microstructure corresponded to austenite (Fig. 157). Steel with carbon from .3 up to about 1 per cent. retains its ferromagnetism after quenching but gives a different microstructure than the slowly cooled steels, this microstructure is that of martensite (Fig. 158), which is characterized by a maze of needles. In the steels with more than 1 per cent. carbon, austenite as well as martensite forms, the needles or patches of the latter being scattered in the grains of austenite.

The austenite is a supercooled γ -iron solid solution, hence it is not ferromagnetic. In the martensite on the other hand it is assumed that the α -iron is the solvent of the carbon, because it is ferromagnetic like the α -iron. With the quenching of the γ -iron solid solution a recrystallization takes place with the formation of the martensite during the transformation of the solvent, but the separation of the carbon as Fe_3C is suppressed (*Stahl u. Eisen* (1912), Nr. 34).

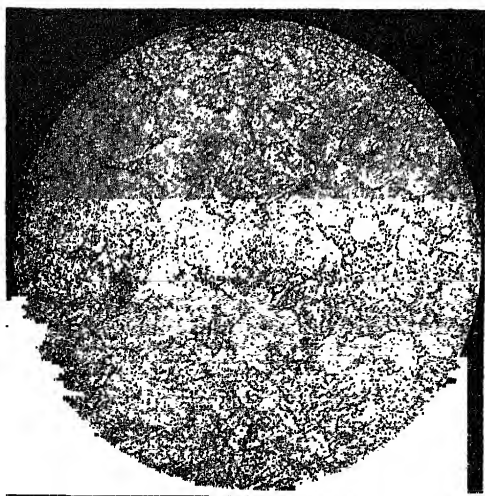


FIG. 160

Iron with 0.5% C. Quenched. Transition occurring from outer edge towards center. Spheres of osmondite surrounded by martensite. Etched with Alcohol + HNO_3 . X 110. From Hanemann (*Stahl und Eisen*, 1906, 778).

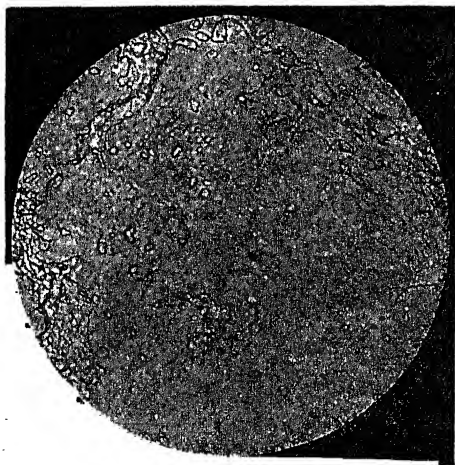


FIG. 159

Iron with 0.9% C, heated for 10 min. 5° above the transformation temperature of pearlite into γ -solid solution and then quenched. Etched with alcohol + HCl. X 1000. From Hanemann (*Stahl und Eisen*, 1912, No. 34, Fig. 23).

The typical appearance of martensite is found only on the surfaces, whose grains have been enlarged through high heat. In a steel which is heated for only a short time and only slightly above the temperature of the loss of its magnetism, the martensite according to Hanemann (*Stahl u. Eisen* (1912), Nr. 34), will not have the typical appearance of that in Fig. 157, but rather that of Fig. 159, in which the ground mass is martensite and the irregular shreds, pearlite. This is formed from small grains of the γ -solid solution and is only slightly perceptible in its needle-like structure. Martensite which is built up like this is known as hardenite. The fineness of its grains gives to the hardenite especially good tensile properties.

If a steel of 0.5 to 1.0 per cent. carbon is quenched in water from a temperature in the γ -area, then its edge consists of martensite and its core, if the piece is not too small, consists of another crystalline variety, which Heyn (*Stahl u. Eisen* (1906), 778) named osmondite. Fig. 160, according to Hanemann, shows the structure of the transition zone of a 0.5 per cent. carbon steel quenched in water. The spherulitic shapes are osmondite and the needle-shaped structure of the ground-mass is martensite. Hanemann (*Stahl u. Eisen* (1912), Nr. 34) claimed these spherulites to be mixtures of α -iron and cementite in submicroscopic division.

One can conceive of the spherulites as a special unstable form of the α -iron group, since they are ferromagnetic. In the γ -solid solutions as much of the martensite as of the osmondite forms upon cooling, but the nucleus number of the martensite is greater than that of the osmondite upon great supercooling, and the linear transition rate of the martensite is greater than that of the osmondite. At both transitions a perceptible change of carbon content does not seem to occur at the concerned limits of transition. It appears accordingly that the two meta-stable forms of the magnetic α -iron do not have a negligible power for dissolving carbon or Fe_3C .

By quenching a steel of 0.9 to 2.0 per cent. carbon, martensite is formed from the cementite needles, while the ground mass consists of the γ -solid solution (austenite) (Fig. 161). At the boundary between the austenite and cementite needles the ability of spontaneous formation of the martensite is considerably greater than in the austenite itself. This phenomenon is quite general. At the boundary of a crystal and its undercooled melt meta-stable forms frequently appear.

(d) Annealing. If martensite and austenite are annealed by increasing the temperature slowly, they approach the slowly cooled stable steels in their properties and structure. The electrical resistance begins to diminish at about 100° and at 500° has reached that of the slowest cooled steels. Here the martensite or austenite loses its carbon content, which separates first as very finely divided temper-carbon and then above 400° passes over into Fe_3C . The decrease in resistance is caused by the separation of the carbon.

The change in volume in the annealing of the austenite and marten-

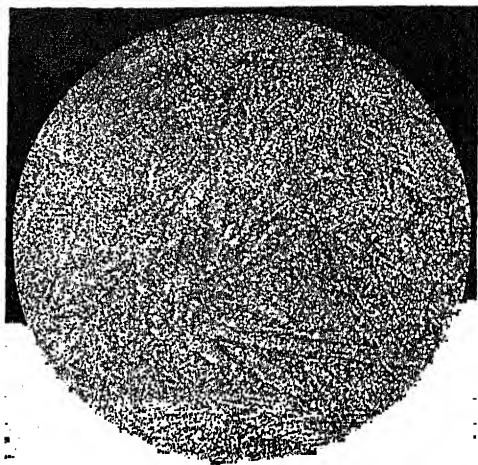


Fig. 162

Martensite with 1.5% C, quenched from 1000°, then heated to 650°. Etched with sodium picrate solution. From Hanemann, l. c., Fig. 10.

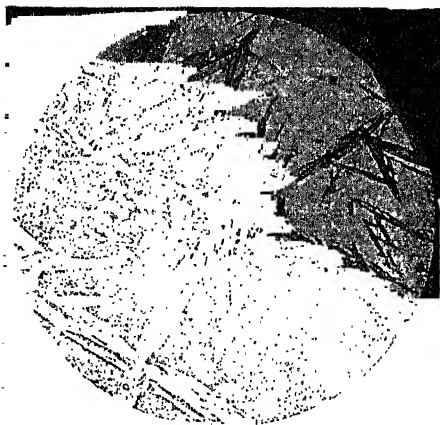


Fig. 161

Iron with 1.79% C. Etched with alcohol + HNO₃. $\times 720$. From Hanemann, l. c., Fig. 15. Austenite as the ground mass. Needles of cementite surrounded by martensite.

site takes place as follows. In the austenite, a recrystallization of the γ -iron into the α -iron occurs after the separation of carbon with an enlargement in volume of about 0.8 per cent., which exceeds the contraction at the separation of carbon. In the martensite due to the separation of carbon, a decrease in volume takes place on annealing while for the steels that contain austenite as well as martensite, an increase in volume occurs between 200 and 300°.

The Brinell hardness and the Scratch hardness decrease with annealing, two constituents are formed, the soft α -iron and the hard cementite.

Fig. 162 shows an annealed martensite structure in which the dissociation is completed. The numerous bright points are cementite, which are imbedded in the α -iron, yet the contours of the original martensite needles can be recognized.

In carbon-steels the γ -solid solutions existing are retained by quenching from high temperatures, and since the hardness always increases through the dissolving of a foreign substance in a crystal, it would be expected, that in such cases hardness will follow quenching. If, however, as in Ni-Si (3-8 per cent. Si), a solid solution can transform into another by slow cooling, without dissociation as with Fe-C, and by quenching from high temperatures the existing solid solution may be conserved, then quenching can also have a softening effect. The slowly cooled Ni-Si alloys with 3 to 8 per cent. silicon, have the hardness of feldspar, while the quenched ones are only slightly harder than calcite.

(e) **Extraction of heat as rapidly as possible.** To produce a crystalline variety which is transformed into another upon its cooling in the supercooled condition at ordinary temperatures it is necessary to extract the heat as quickly as possible by which the transformation-centers are prevented from forming or growing.

If a piece of metal at a high temperature is inserted into a series of liquids, the rate at which the temperature of the piece diminishes is not proportional to the conductivity of the concerned liquid, but rather as C. Benedicks (*Journ. Iron and Steel Inst.* 77, 153 (1908)) has shown proportional to its specific heat, since the piece produces convection currents in the liquid and the amount of heat conveyed from this is usually under the same condition proportional to the specific heat of the unit volume of the liquid.

If the piece of metal was heated so high that at its surface the liquid was heated to its boiling point, then bubbles of vapor would arise from the cooled surface. Above the temperature of the piece of metal at which the vapor begins to generate the rate of cooling is not proportional to the heat content of the unit of volume of the liquid but to the heat of vaporization of the liquid (Benedicks). Since water is characterized by its great volume-heat and its great heat of vaporization, consequently quenching in it is especially rapid.

(f) The forms of iron.

TABLE 32

The Forms of Iron	Transformation Point	Heat of Transformation per 1 gm.	Volume Change per 1 gm.	Magnetizability
Meta-stable	Liquid			
	↑ δ	1510°	—	>0
				Non-magnetic
Austenite *	↑	1401°	0.5? cal.	?
non-magnetic	↑ γ			
	↑ β	906°	2.9 "	— 0.001 ccm.
α'-Osmondite	↑			
ferromagnetic				
α"-Martensite	α	769°	1.7 "	0.0000 "
ferromagnetic				
				Exceedingly weak
				Strongly ferromagnetic

* Undercooled γ-Fe.

From the measurements of the relation of length to the temperature for almost pure iron the linear contraction at the transformation of α-iron into γ-iron, was found to be 0.26 per cent. at 760°, hence 0.78 per cent. for the cubical or 0.001 cm.³ per gm. Following the transformation of the austenitic steel of 2 per cent. carbon and 2 per cent. manganese into martensite steel by cooling in liquid air, Maurer (*Metallurgie* 6, 33 (1909)) found a cubical expansion of 2.31 per cent. at 20°. To determine, if this last change in volume corresponded to that of the γ- into α-iron at 20°, it would be necessary to know the volume isobars of the γ- and α-iron from 760° down to 20°.

(g) The transformation of austenite into martensite by cooling in liquid air. If austenite is cooled in liquid air, then according to Osmond it will take the structure of martensite and will be ferromagnetic. The equilibrium temperature of austenite with martensite of the same composition must lie a little lower than the equilibrium temperature of austenite with pearlite or a little below 720°. Above this temperature the austenite is more stable than the martensite; at lower temperature the martensite is more stable than the austenite. The transformation of austenite into martensite, however, appears only at strikingly low temperature and indeed this transformation appears to take place from relatively few transformation-centers with an appreciable linear velocity.

(h) The influence of pressure on the transformation temperatures of iron. In a completely reversible equilibrium, the direction of the equilibrium curve $\frac{dT}{dp}$ can be calculated from the change in volume Δv and the heat of transformation r_p : $\frac{dT}{dp} = \frac{\Delta v T}{r_p}$. For the

relation of the equilibrium temperatures of the several forms of iron the following values are obtained:

$\frac{dT}{dp}$ for the transformation of γ - into β -iron -0.009° for 1 kg. per 1 sq. cm.; and,

$\frac{dT}{dp}$ for the transformation of β - into α -iron 0.0000° for 1 kg. per 1 sq. cm.

By increasing the pressure, the transformation temperature of γ - into β -iron is moved to lower temperatures and that of β - into α -iron is not changed perceptibly, because the change in volume at this transformation is extremely small.

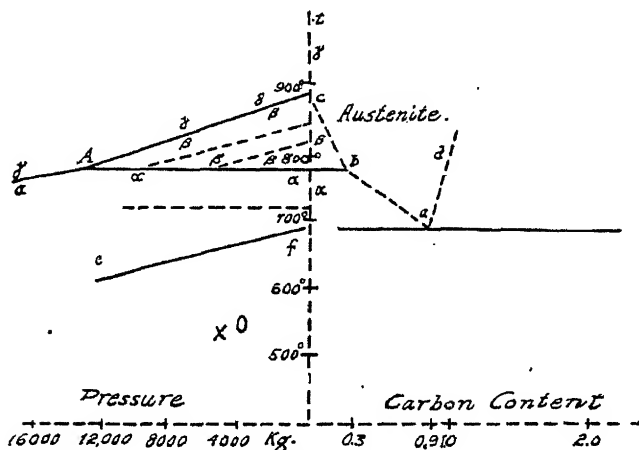


FIG. 163

These two transformation lines are indicated in Fig. 163, they intersect at the point A, at 12000 kg. per 1 sq. cm. A third transformation curve must go through at this point, at which γ - and α -iron are in equilibrium with each other. With a pressure over 12000 kg. the γ -iron transforms directly into α -iron.

Even the influence of pressure on the transformation of saturated γ -solid solutions with 0.9 per cent. carbon into pearlite at 720° can be calculated by the above formula, since this equilibrium is complete. From Charpys' data, this transformation gives Δv as -0.00048 , and r_p becomes 2 cal. per gm. of iron, which in the formula $\frac{dT}{dp}$ becomes -0.0054° per kg. This value corresponds to the line $e f$ in Fig. 163.

The influence of the carbon content on these equilibria is also indicated in Fig. 163. If one can imagine this portion of the

figure rotated 90° around the t-axis, the diagram of β -iron in the pressure-temperature-concentration space is represented by a tetrahedron. The effect of the pressure on the equilibrium temperature is analogous in many respects to that of the carbon content. Roberts-Austen (*Inst. of Mechanical Engineers* (1893)) has determined the cooling curve of a block of steel of 0.9 per cent. carbon under a pressure of 1 and 4700 kg. per sq. cm. and found the arrest under 1 kg. pressure at 690° , and for 4700 kg. at 560° , indicated by point O, Fig. 163. The duration of the latter arrest was perceptibly smaller than that of the arrest under 1 kg. pressure. The lowering of the transformation point would then be found to be about five times greater than that corresponding to the calculated transformation line. Consequently the transformation line may slope considerably towards the pressure axis, because with increasing pressure, Δv increases and r_p decreases; these deviations can also take place so that the point O will lie on another equilibrium curve, that of the γ -solid solution and a compact form of iron, stable only for high pressures. In the last case a second transformation point must become noticeable. Which of the two possibilities would prove to be correct would be of interest in pursuing this question further as it would either lead to the production of a denser iron or to a new method for the hardening of iron.

Since modern Seismology, as is well known, has confirmed the old supposition that the earth was apparently rich in iron. It can also be concluded that a great increase in density occurs at the depth of about 1500 km. (Wiechert). At this depth the pure iron must exist in the nonmagnetic state. Since at a depth of 64 km. a temperature of 600° at 16000 kg. per sq. cm. apparently prevails, then the pure iron existing at a depth greater than 64 km. must be nonmagnetic, which also applies to iron containing nickel, manganese, silicon and carbon.

2. Iron-Silicon.

The equilibrium diagram, Fig. 164, is taken mostly from the data of Guertler and Tammann (*Zeitschr. f. anorg. Chem.* 47, 163 (1905)). T. Murakami (*Science Reports*, Tohoku Univ., 10, 79 (1921)) and Kurnakow and Urasow (*Zeitschr. f. anorg. Chem.* 123, 89 (1922)). The constituents crystallizing from the melts are a series of solid solutions in γ -iron from about 2.5 to 21.5 per cent. silicon, the compound FeSi, a series of solid solutions from 55.2 to 61.5 per cent. silicon and finally practically pure silicon. The melts with 55.2 to 61.5 per cent. crystallize at an almost constant temperature which is the same for each of the melts. After the separation of the FeSi from the melts with more than 33.6 per cent. silicon, the crystallization will terminate with the formation of the saturated solid solution at 55.2 per cent. silicon and after the separation of silicon with that of the solid solutions containing 61.5 per cent. silicon.

From the low silicon melts (less than 2.5 per cent.) solid solu-

that this transformation disappears at a silicon content of 27 per cent. Since on formation of Fe_3Si_2 at 1020° , there generally remains some of the constituent c , an accurate determination of the composition of the constituent claimed to be Fe_3Si_2 presents considerable difficulty.

3. Iron-Nickel.

Arrests are found on the cooling curves for all compositions of the iron-nickel melts, and the alloys obtained consist of crystallites which are homogeneous throughout. Perceptible dissociation is apparent neither at the crystallization nor at the transformation occurring

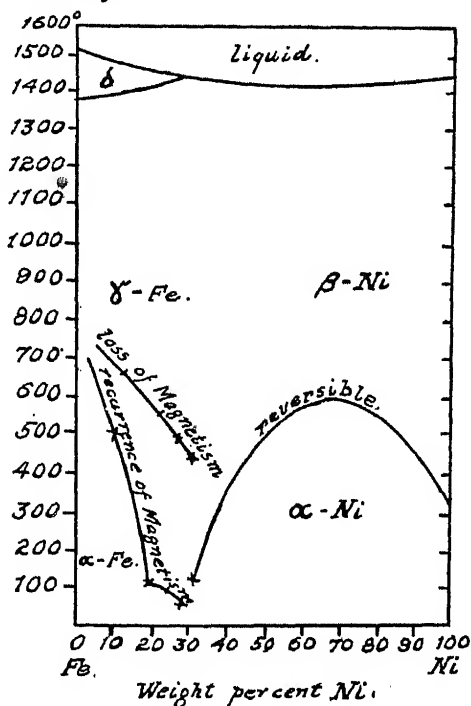


FIG. 165

at lower temperatures at which the alloys, like their components, Fe and Ni, become magnetic. This lack of dissociation on crystallization and transformation is characteristic of the alloys of the three ferromagnetic metals iron, cobalt and nickel (p. 196). These three elements are as closely related to each other in the metallic state as any other two metals.

The behavior at the loss and at the recurrence of their magnetization divides the Fe-Ni alloys into two groups. In the alloys with 0 to

30 per cent. nickel, the loss of magnetism takes place at a considerably higher temperature upon heating, than the recurrence upon cooling. This irreversibility may depend on the overstepping of the true unknown equilibrium curve of the γ - and α -solid solutions. The transformation is reversible in the nickel steels from 30 to 100 per cent. nickel. Fig. 165 shows the location of the reversible and irreversible transformations. The magnetic permeability disappears and returns almost discontinuously, similar to pure nickel and iron. A gradual disappearance of magnetizability is apparent only in the alloys with 30 to 40 per cent. nickel.

4. The Ternary Carbon Steels.

By adding increasing amounts of Ni, Mn, or W to a carbon steel, pearlite is no longer formed upon slow cooling, but the structure becomes martensitic and for still greater additions it becomes austenitic. For each carbon content there is a definite amount of addition at which martensite or austenite will appear. For additions of nickel, Fig. 166 indicates the carbon content, at which according

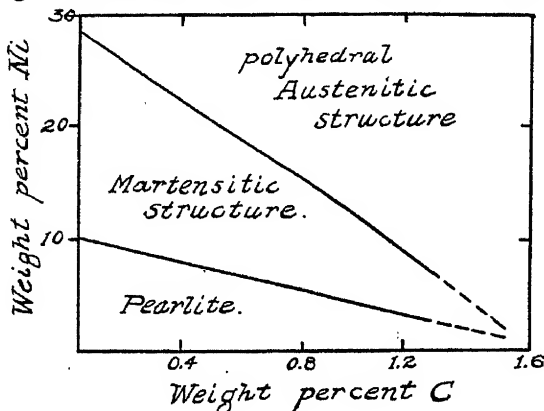


FIG. 166

to Guillet (*Aciers Spéciaux*, Paris (1905)) these changes in structure occur. Similar diagrams have been obtained for the additions of Mn, Cr, W, etc. The steels with martensitic structure are known as self hardening, as they become hardened without being quenched. The steels with austenitic structure are known as naturally hard, because this condition is stable at ordinary temperatures, while for the carbon steels the austenitic condition is unstable. The temperature of the pearlitic transformation is lowered below the ordinary temperatures by these additions.

The high speed steels (G. Mars, *Die Spezialstähle*, Enke, Stuttgart

(1912)) have a still more complicated composition having in addition to 0.5 to 1.0% C, 5% Cr and 20% W. The formation of pearlite is also suppressed by additions in these steels, the carbon being dissolved in the ground mass. High speed steels are characterized by their ability to retain their hardness even between 500 and 600°, so that they may be used during machining operations where the tool becomes strongly heated.

5. Meteoric Nickel-Iron.

The nickel content of meteoric-iron varies between 4 and 26.5 per cent. but is seldom over 20 per cent. or below 5.5 per cent. Meteoric-iron shows on a fractured surface large octahedrons which are quite uniform. (Osmond, *Compt. rend.* 118,, 532.—*Revue de Metallurgie* (1904) 64; F. Berwerth, *Wiener Sitzb.* (I) 114, 345 (1905); Fraenkel u. Tammann, *Zeitschr. f. anorg. Chem.* 60, 416 (1908); C. Benedicks, *Nova Acta R. Soc. Scient. Upsalensis*, Ser. IV., Vol. 2, Nr. 10 (1910); F. Berwerth u. Tammann, *Zeitschr. f. anorg. Chem.* 75, 145 (1912).)

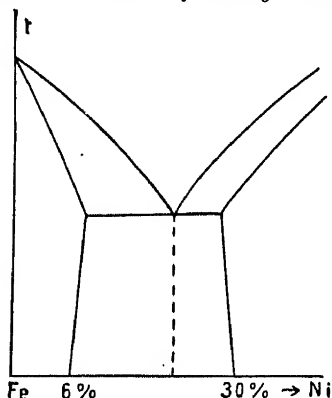


FIG. 167

The low nickel constituent of meteoric-iron, camazite, occurs in hexahedrons which are arranged parallel to the four pair of surfaces of the octahedrons. The camazite is surrounded by plates high in nickel, taenite. Between the camazite sections enclosed by the taenite, are spaces of various sizes, which are filled up with plessite. This possesses quasi-eutectic structure, with camazite as the ground mass in which the taenite is distributed more or less regularly. The amount of plessite and of the primary camazite surrounded by taenite is subject to quite considerable variations, because in many meteors only the plessite appears, in others only primary camazite appears.

Osmond and Roozeboom have attempted to connect the origin of the meteoric structure with the transformation of α -iron-nickel into

γ -iron-nickel; although a dissociation due to this transition has not been observed in the crystallites of technical nickel-iron. Hence they assume that when this transformation took place very slowly as in the course of geological epochs, the dissociation occurred and gave the recognized meteoric structure corresponding to the phase diagram (Fig. 167). One must however admit that this is an ad hoc hypothesis, since it finds no basis in the observations of transformation of nickel-iron either technical or meteoric.

In the technical nickel-iron, the recurrence of the magnetizability is not accompanied by any appreciable dissociation and in the meteoric



FIG. 168

Heated for 7 hrs. at 1000° .
X 68. From Damaraland.



FIG. 169

Heated for 15 hrs. at 1000° .
X 67. From Damaraland.

the loss of magnetizability by no perceptible dissolving of taenite in the camazite, and in the camazite the transformation proceeds entirely irreversibly as in the technical nickel-iron.

Add to this the facts found by Berwerth, that camazite on annealing dissociates into the crystallites of technical nickel-iron. Even at 400° these grains appear in camazite although slowly. It is magnetic at this temperature, the magnetizability is lost between 600° and 700° but returns again at 550° to 450° .

The change of meteoric nickel-iron into the technical nickel-iron can be easily followed microscopically. If a piece of meteoric iron is melted, it cannot be differentiated from the technical nickel-iron. At low temperatures this transformation proceeds very slowly, and it is interesting to follow. Fig. 168 shows a piece of meteoric iron from Damaraland after heating at 1000° for a period of 7 hours. The granulation (bright) in the camazite is distinct. The taenite (bright

seams of the darker plessitic area) is still preserved. After a further heating of 8 hours at 1000° , the granulation in the camazite becomes more distinct and the excess of nickel diffuses from the taenite into the camazite (Fig. 169).

Structures similar to the macrostructure of meteoric iron have been observed by J. O. Arnold and A. McWilliam (*Nature* 71, 32 (1904)) as well as by Belajew (*Revue de Metallurgie* (1910)) in the microscopic crystallites in nickel-iron produced aluminothermically and cooled as slowly as possible.

It may be further urged against the equilibrium theory of Osmond and Roozeboom, that the nickel content of the camazite and taenite is not constant as would be expected for two crystalline varieties in equilibrium. The nickel content of the camazite varies between 4.8 and 7.2 per cent. and that of the taenite between 23.6 and 35.5 per cent.

The origin of the meteoric structure may be conceived of as follows. The camazite crystals formed first, and at their boundaries a high nickel mixture of iron and all the impurities of the camazite crystals collected. At these boundaries the interstitial substance is precipitated with the formation of taenite. By the lamellae of the interstitial substance the diffusion of the nickel from the taenite into the camazite is prevented. Corresponding to the size of the camazite grains the meteoric iron must have crystallized slowly. In the fall of the meteorites the interstitial substance is lost and then by reheating, the diffusion of the nickel from the taenite to camazite may take place. Moreover it is favored considerably by the recrystallization on reheating. This first occurs by reheating to 400° .

6. Copper-Tin.

The complicated equilibrium diagram of the copper-tin alloys has been investigated many times. Although it has been established mostly upon the basis of the work by Heycock and Neville (*Phil. Trans.* 202A (1904)) there are individual points which even after the later investigations by Shepherd and Blough (*Journ. phys. Chem.* 10, 630 (1906)) as well as by Giolitti and Tavante (*Gazz. chim. ital.* 38, II, 209 (1908)) have not been cleared up completely. The diagram, Fig. 170, has been drawn up by Bornemann after a critical review of the previous investigations. (*Die Binären Metallegierungen* I, 32, Knapp, Halle (1909).) The liquid copper-tin mixtures can be in equilibrium with six different crystalline varieties depending on the copper content. These equilibria are shown by the two curves, whose points indicate the compositions of the melts and of the crystalline varieties in equilibrium with them. A parallel to the concentration axis intersects these lines at two points, one of which indicates the composition of the melt and the other the composition of the crystalline variety in equilibrium with the melt.

The completion of the crystallization is shown in this diagram by the dotted lines 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12. By these lines the fields of existence within which liquid mixtures are capable of existing with one crystalline variety are separated from fields of existence within which the last remainder of the melt has disappeared.

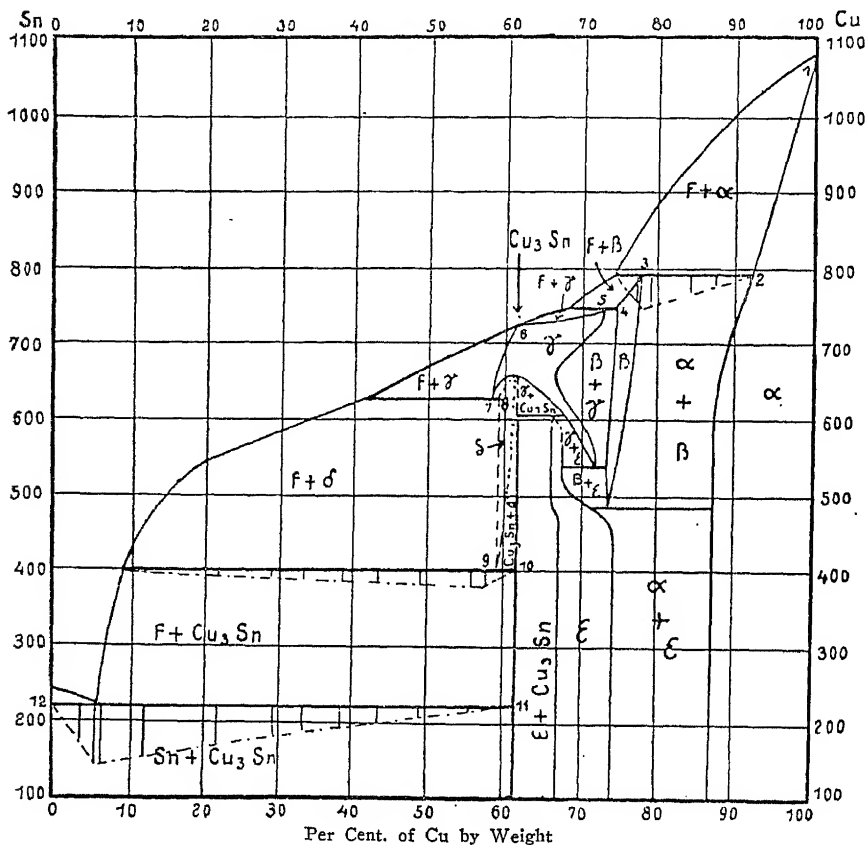


FIG. 170

The curve 5, 6, 7, which touches the curve of the beginning of crystallization at the point 6, describes the completion of the crystallization of the γ -solid solution. At this point of contact, 6, the tangents to the curves of the beginning and completion of crystallization are horizontal. The concentration at this point corresponds to the formula Cu_3Sn . The γ -solid solution may accordingly be regarded as a solution of copper or tin in the space lattice of the compound Cu_3Sn . At 650° this space lattice changes into another and the result of this

is that a dissociation of the γ -solid solution appears. This dissociation is quite perceptible in the γ -solid solution with more copper than corresponds to the formula Cu_3Sn . However a little above 600° , the two crystalline varieties, γ - and Cu_3Sn combine again to form the crystalline variety ϵ .

The saturated solid solutions 3 and 2 are in equilibrium with a definite melt at the temperature of the horizontals 2, 3. They are, however, also in equilibrium with each other and this equilibrium continues with decreasing temperature, because the two saturated solid solutions continue in the interchange of material. This interchange of material takes place either as a result of the diffusion between the intimately mixed crystallites of the two saturated solid solutions whereby the one grows at the expense of the other, or by the formation of one saturated solid solution in the lamellae of the other.

As a rule this interchange between two solid solutions is very limited, but is quite perceptible here. The interchange for the saturated solid solutions 5 and 4 is especially large. The γ -solid solution, 5, becomes poorer in copper through the separation of the saturated β -solid solution, but then becomes richer in copper again after the resolution of the saturated β -solid solution.

If the curves of the saturation of a solid solution in two other crystalline varieties intersect, then the mutual solid solution disappears at temperatures above or below the temperature of the intersection point of the two equilibrium systems. If its dissociation into two other saturated solid solutions takes place with evolution of heat, then the field of existence of the dissociated solid solution lies above the temperatures, if it takes place with heat absorption, it lies below the equilibrium temperature of the three crystalline varieties.

In the copper-tin alloys, three different crystalline varieties, β , γ and δ -solid solutions disappear upon slow cooling. These solid solutions dissociate into two other saturated solid solutions at definite equilibrium temperatures or into a crystalline variety and a melt existing in equilibrium with it. The β -crystal dissociates into α - and ϵ , the γ on the one hand into β - and δ -crystals, on the other hand at 620° into δ -crystals and a melt with 42 per cent. copper, and the δ -crystals at 400° into Cu_3Sn and the melt with 9 per cent. copper. Whether the saturated δ -crystal splits off the melt on cooling from 620 to 400° and thereby becomes richer in copper, depends on the course of the line 8-9. When the point (8) lies at a greater concentration of copper than the point (9) that will not be the case, not even when both points have the same copper concentration, but will be true when the copper concentration of the point (8) is smaller than that of point (9).

As a result of the disappearance of the crystalline varieties β , γ and δ , the building up of the copper-tin bronzes is quite simple after slow cooling to ordinary temperatures. The bronzes with more than 87 per cent. copper consist of homogeneous crystallites, the bronzes

with 74 to 87 per cent. copper consist of the saturated α -crystal and the saturated ε -crystal, which is subject to less oxidation than the α -crystal. The bronzes with 67 to 74 per cent. copper are in return built up of homogeneous crystallites. The bronzes with 62 to 67 per cent. copper contain the crystalline varieties ε - and Cu_3Sn , and the alloys poor in copper, according to the diagram, consist of Cu_3Sn and tin. However in the alloys with more than 40 per cent. tin, a crystalline variety appears which contains a little more copper, corresponding to the formula CuSn . With regard to the formation of this crystalline variety nothing is given in the diagram, because the investigations indicate a probable unstable crystalline variety.

If one quenches the copper-tin alloys which contain more than 40 per cent. copper from a temperature above the last transformation, its microstructure will change and correspond to that indicated in the equilibrium diagram. The quenched bronzes are in general softer than those cooled slowly. A tuning fork of quenched bronze gives a deeper tone than a slowly cooled tuning fork. The tensile strength and elongation through tension is greater in the quenched bronzes than in those slowly cooled. The great elongation of copper decreases very much with small additions of tin, so that the ductility of bronzes is also poor.

7. Copper-Zinc.

The equilibrium diagram of these alloys has been worked out by Roberts-Austen (*Proc. Inst. Mech., Eng.* (1897), 31), Shepherd (*Journ. phys. Chem.* 8, 421 (1904)) and Tafel (*Metallurgie* 5, 349 (1908)) and the important parts of these determinations are shown by Bornemann (*Die binären Metallegierungen* I, Halle (1909), p. 16) in Fig. 171. The curve of the beginning of crystallization consists of six branches; the crystallization is completed at the temperature of the dotted lines 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12. It is characteristic of the copper-zinc solid solutions, which appear in the same conglomerate, to change their composition with change of temperature. Thus the alloys of 65 per cent. copper, which at 900° consist of almost equal amounts of saturated solid solutions 2 and 3 become homogeneous upon cooling, because the solid solution 3 is absorbed by the solid solution 2. The temperature at which this occurs is taken from the diagram. To determine this temperature it is only necessary to erect a perpendicular at the point of concentration, 65 per cent. copper, and its intersection with the saturation curve of the solid solution 2 will be the temperature. This gives the temperature for the disappearance of the solid solution 3 as about 750° . By successive heating and quenching the temperature at which a saturated solid solution disappears, may be established, the alloy thus becomes homogeneous according to microscopic investigation.

On the other hand a homogeneous conglomerate at a higher temperature can become inhomogeneous upon cooling. Thus the alloys

of 58 per cent. copper consist of homogeneous crystallites above 700° , but below 700° , lamellae of the solid solution 2 form in amounts increasing with decreasing temperature.

In the solid solutions, lamellae of the ϵ -solid solution form by cooling and after this separation the remaining saturated δ -solid solution finally dissociates at 450° into the two saturated solid solutions γ and ϵ .

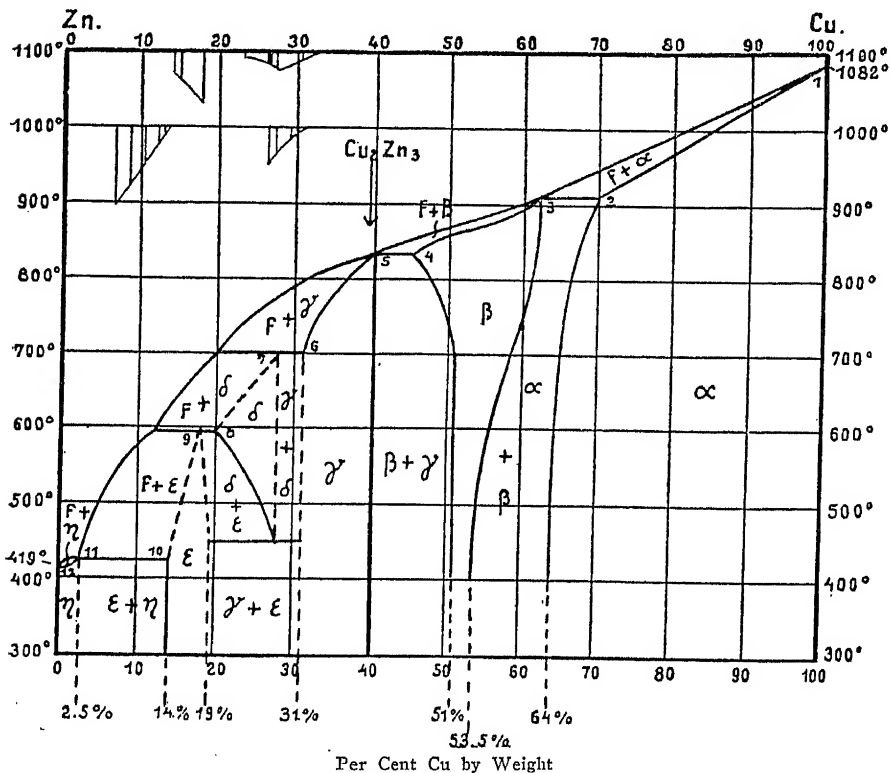


FIG. 171

After cooling to room temperature nine series of alloys may be differentiated consisting alternately of one and two constituents. The limits of these series can be easily determined from the diagram. Yellow brass of 70 per cent. copper consists of the α -solid solution. Frequently other metals are added to the mixture in varying amounts. The β -solid solution differs from the yellow copper-rich α solid solution by its red color. The alloys with more than 60 per cent. zinc are grayish.

Opinions are divided as to what zinc-copper compounds really exist.

8. Copper-Nickel.

Copper and nickel are miscible with each other in all proportions in the liquid as well as in the solid states. (Guertler u. Tammann, *Zeitschr. f. anorg. Chem.* 52, 25 (1907).) Fig. 172 gives the equilibrium diagram. At the ordinary cooling rate two varieties of crystallites of different composition are found in the alloys, the primary crystallites rich in nickel, surrounded by a ground mass rich in copper. Frequently it is noticed that the nickel content changes gradually at the edge of both crystalline varieties. By slower cooling this concentration difference is effaced and after a long period of heating to a temperature not much below that on the curve for the completion of crystallization, they disappear completely.

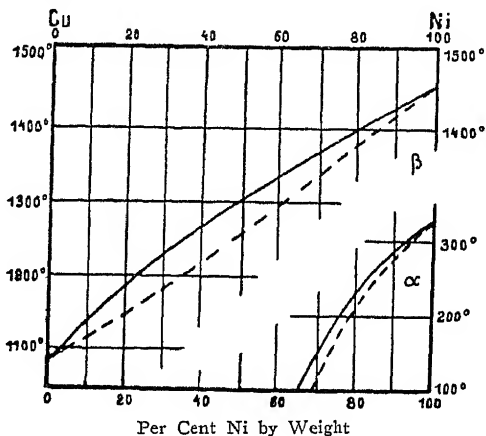


FIG. 172

The temperature for the loss of ferromagnetism of nickel is lowered by copper. The curve for this transformation cuts the line parallel to the concentration axis for the temperature of 20° at about 55 per cent. nickel. Consequently the alloys from 0 to about 55 per cent. nickel at this temperature are non-magnetic, while the alloys rich in nickel are magnetic. Ferromagnetism appears ordinarily upon cooling about 20° lower than when it disappears upon heating which is explained by the supercooling of a transition with which the recurrence of magnetism is connected.

At ordinary temperatures the nickel-copper alloys consist of two series of solid solutions, those that are non-magnetic, whose molecules are arranged in the space lattice of copper and β -nickel, and those that are magnetic, whose molecules are arranged in the space lattice of magnetic nickel. Accordingly the properties of each series must establish a curve for each, which will intersect at the concentration of the limits of the two series of solid solutions. Feussner and

Lindeck (*Abhandl. d. Phys. Techn. Reichsanstalt* 2 (1895) (*vgl. Ann. d. Phys.* 32, Taf. 11, 1910)) found that the electric conductivity as well as the thermal force in relation to the concentration may be represented by two curves, whose intersection lies approximately between 50 and 45 per cent. nickel. That the limit of the two series of alloys as determined on the basis of their magnetic susceptibility vary somewhat from these limits is perhaps attributable to insufficient homogeneity of the alloys, which have been investigated magnetically.

9. Copper-Silver.

The copper-silver alloys have been investigated by Heycock and Neville (*Phil. trans.* 189A, 25 (1897)), Friedrich and Leroux (*Metal-lurgie* 4, 297 (1907)) and Lepkowski (*Zeitschr. f. anorg. Chem.* 59, 285 (1908)). The two metals are miscible in the liquid state in all proportions, in the crystalline state however silver dissolves only 4.5 per cent. copper and copper only 5.5 per cent. silver (Fig. 173). A silver-copper compound does not separate out. The fine grained eutectic contains 28 per cent. copper. By ordinary cooling some eutectic

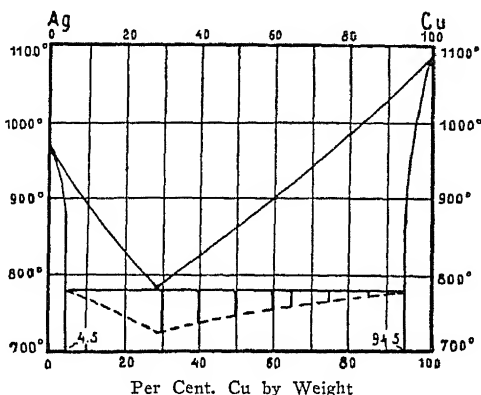


FIG. 173

will be found in an alloy of 1 per cent. silver and likewise with an alloy of 3 per cent. copper. However if the silver-rich and copper-rich alloys are heated for about 80 hours at 700°, the remainder of the silver existing in the eutectic diffuses into the copper crystals and the remainder of the copper existing in the eutectic diffuses into the silver crystals. After 80 hours of heating the silver crystals finally contain 4.5 per cent. of copper and the copper crystals 5.5 per cent. of silver. The solid solutions formed by ordinary cooling are, however, considerably lower in copper or silver, than those of the annealed alloys. Since upon long heating the composition of the primary solid solution will change, likewise a change will take place in the components

of the eutectic. Hence the composition of the eutectic will be displaced slightly and the eutectic temperature will increase a little.

10. Copper-Gold.

It has been well established by Kurnakow and Žemcžužny (*Zeitschr. f. anorg. Chem.* 54, 149 (1907)) that these two metals are entirely miscible in the liquid and solid states. The curve of the beginning of crystallization has a very pronounced minimum, where it coincides with the curve for the completion of crystallization (Fig. 174). For the ordinary rate of cooling the crystallites of the solidified alloys are not homogeneous. In the alloys from 0 to 82 per cent. gold, the

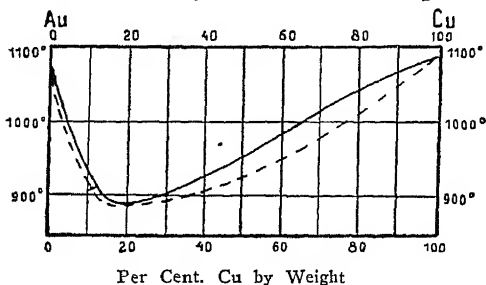


FIG. 174

center of the crystallites is richer in copper than the peripheral layer; in the alloys from 82 to 100 gold, this non-uniform distribution is reversed. The basis for this may be readily seen from the diagram. From the copper-rich melts the solid solutions which separate first are richer in copper than the melt and since the rate of diffusion of the gold into this solid solution is insufficient, the remainder of the melt becomes higher in gold. At the crystallization of gold-rich melts, the relations are reversed, the center of the cored crystals is consequently richest in gold. By heating the alloys, the cored crystals become homogeneous.

11. Gold-Silver.

Gold and silver are also miscible with each other in all proportions in the liquid and crystalline states. The curves of the beginning and completion of crystallization are given in the diagram, Fig. 175 (Jänecke, *Metallurgie* 8, 599 (1911) and Raydt, *Zeitschr. f. anorg. Chem.* 75, 58 (1912)). For the ordinary rate of cooling the alloys consist of cored crystals, whose gold content decreases a little towards the exterior, however, the difference here is much smaller than in the copper-nickel and gold-copper alloys. No etching reagent has been developed yet, which will develop the structure of the silver-gold alloys

with more than 80 per cent. gold. By slight deformation of these alloys, the slip lines appear quite distinct for the individual crystallites on a polished surface, so that in consequence of the resulting lines, the outline of the crystallites may be recognized.

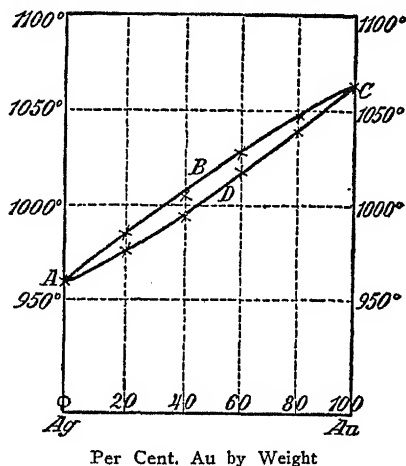


FIG. 175

12. Lead-Tin.

If small amounts of liquid lead-tin alloys are cooled in the ordinary manner, lead containing a little tin (about 2-4% Sn) will crystallize out from the liquid mixtures of 0 to 65 per cent. tin, and from

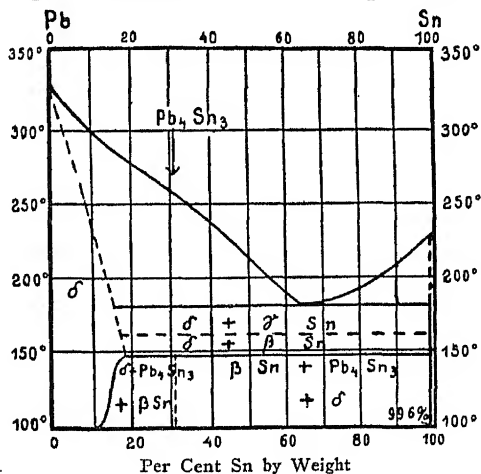


FIG. 176

liquid mixtures of 65 to 100 per cent. tin, tin containing very little lead (a little less than 0.4 per cent. lead) will crystallize. If after the separation of lead or tin, the remainder of the melt has reached the eutectic concentration of 65 per cent. tin, it will crystallize eutectically in small crystallites of lead low in tin and tin low in lead. At 160° the γ -form of tin formed from the melt transforms into the β -form with a small change in volume. This transformation is perceptible in a large number of the alloys by a characteristic sound. On account of this, the structure of the alloys which are frequently used as solder will be somewhat loose. If it is desired to solder at the lowest possible temperature in order not to heat the pieces to be joined too high, it is recommended that the eutectic alloy which melts at 181° be used. As a rule when this is not important, the cheaper lead-rich alloys can be used in which the looseness due to the transformation of the tin is less, corresponding to the lower tin content.

By very slow cooling (Rosenhain and Tucker, *Phil. Trans.* 209A, 89 (1908)) the lead crystals take up considerably more tin than upon rapid cooling and moreover a compound forms slowly from the solid solution with 18 per cent. tin and that with 99.6 per cent. tin, which perhaps corresponds to the formula, Pb_4Sn_3 , Fig. 176.

13. Magnesium-Aluminum.

The alloys rich in aluminum form with additions of magnesium the alloys known as "Magnalium." The alloys rich in magnesium are employed where strength and lightness are required. The equilibrium

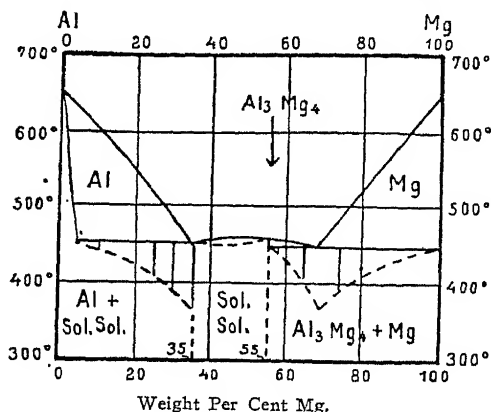


FIG. 177

diagram (Grube, *Zeitschr. f. anorg. Chem.* 45, 225 (1905)), Fig. 177, indicates that a compound, Al_3Mg_4 , separates from the melt, and that this compound forms with aluminum, a series of solid solutions, in

which aluminum can dissolve up to 20 per cent. The solid solutions crystallize in a very small temperature interval; only arrests are found on the cooling curves. Corresponding to their crystallization, the alloys of 35 to 55 per cent. magnesium consist of homogeneous crystallites, while the alloys of lower magnesium content consist of the solid solution with 6 per cent. magnesium (Vogel, *Zeitschr. f. anorg. Chem.* 107, 268 (1918)) and the solid solution with 35 per cent. magnesium. In these solid solutions, the ground mass of the alloys with 0 to 35 per cent. magnesium, very small amounts of Al_3Mg_4 may be dispersed. The alloys with more than 55 per cent. magnesium consist either of the primary compound or of the primary magnesium, which frequently appear as hexagonal stars; both are surrounded by the eutectic $\text{Mg} + \text{Al}_3\text{Mg}_4$.

14. Tin-Antimony.

The equilibrium diagram of the tin-antimony alloys has been investigated repeatedly. In the following discussion, only that of R. S. Williams (*Zeitschr. f. anorg. Chem.* 55, 14 (1907)) will be considered, since it has shown a close agreement between the thermal phenomenon and the structure of the alloys. The equilibrium diagram, Fig. 178, indicates that antimony and tin are miscible in the liquid state in all proportions and form three series of solid solutions with each other. The limits of these series are 0 and 8, 49.8 and 52.8, 90 and 100 per cent. by weight of antimony. The solid solutions between 49.8 and 52.8 per cent. antimony are considered as solid solutions of the compound SnSb with excess antimony. They crystallize in well formed cubes.

The antimony-rich solid solutions react at 420° with the melt B with the formation of the saturated solid solution b . Here, however, there seems to occur a complete enveloping of the needles of the antimony-rich solid solutions a by layers of the solid solutions b . Consequently at 420° the reaction is not completed and the remainder crystallizes at 243° . If the alloys whose composition lies between b and a are heated for 16 hours at 360° , the tin of the remainder of the melt diffuses through the layer of the enveloping b -crystal into the antimony-rich solid solution, and the reaction is thereby completed. The alloys consist then of the two crystalline varieties b and a , and evolution of heat at 243° no longer occurs. The alloys whose composition lies between B and b contain after the normal cooling of their melts, a little of a and a little of the mixtures of the crystalline varieties d and c . By a longer heating at 360° they become completely homogeneous.

The alloys, whose composition falls between the points c and d , consist of two crystalline varieties, the compound, SnSb (c) and the tin-rich solid solution d . Those richest in tin containing less than 8 per cent. antimony consist of homogeneous crystallites.

Between 10 and about 80 per cent. tin according to the data of Gallagher (*Journ. of Phys. Chem.* 10, 93 (1906)) a feeble evolution of heat occurs at 313° to 319° . According to Konstatinow and Smirnow (*Ber. Petersb. Polytechn. Inst.* 15, 141 (1911)) the same occurs

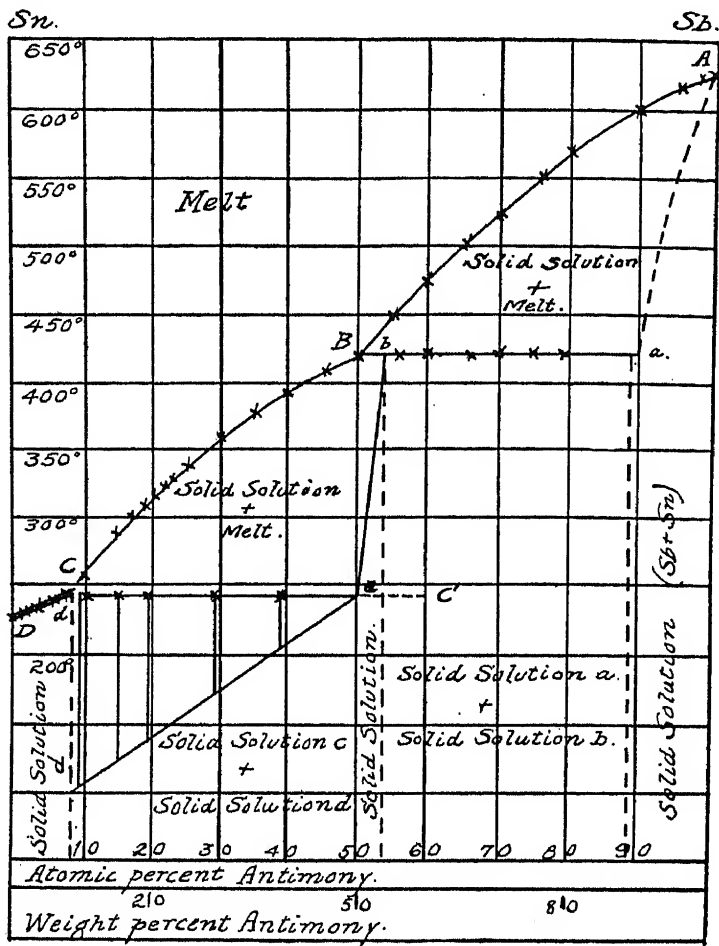


FIG. 178

for the homogeneous alloys only between 50 to 80 per cent. tin at 319° . Accordingly the compound Sb_2Sn_3 should form at 319° from SnSb and the melt with about 80 per cent. tin. If tin and antimony are melted in a narrow glass tube in such a way that the tin and antimony are stratified, it is possible to prepare a uniform concentration

gradient from antimony to tin. On a section parallel to the axis of the resulting cylinder, the entire series of possible structures of the alloys of antimony and tin will be seen according to Williams' diagram. This method due to Le Chatelier is of considerable importance in the working out of a partial diagram of a ternary system, when sufficiently uniform concentration gradients can be produced in the melts.

The alloy with 8 to 9 per cent. antimony, Britannia metal, is considerably harder than tin, but is still plastic. The alloy with 20 per cent. antimony which contains hard cubes of the compound SnSb in the soft ground mass of the tin-rich solid solutions d , is used as anti-friction metal. The antimony-lead alloys, in which hard crystallites of antimony are deposited in a soft cushion of lead, or better a eutectic of lead-tin, also serve this purpose. Barium-lead alloys with 2 to 4 per cent. barium, are also employed as bearing metals.

G. The Physical Properties of Binary Alloys

1. The Specific Volume in Relation to the Composition.

We can construct surfaces for the heat content of mixtures of two substances, which exhibit the relation of the heat content to the composition and temperature; it is possible to obtain similar surfaces for specific volume. The surfaces of heat content and specific volume must be very similar to one another, since the projection of their discontinuities and edges on the temperature-composition planes must give identical equilibrium diagrams for the same two substances (pp. 33, 149 and 174). By measuring the specific volumes of definite mixtures in relation to the temperature, it is possible to get results similar to those obtained by the determination of the cooling curve. However the cooling curve determination is selected because it is carried out much easier at high temperatures, than the determination of the curve of specific volumes in relation to temperature.

If a thermal effect is doubtful on the cooling curve, it can often be easily confirmed, by the determination of the volume isobars. There are transformation points with very small changes of heat contents, which correspond to quite large changes in volume.

The determination of volume isobars of substances and of their mixtures especially at high temperatures, meets with considerable difficulty, because on crystallization and transformation, interstices form between the crystallites of the conglomerates, which exert a considerable influence on the specific volume. By hammering and pressing, these interstices can probably be closed, but in consequence of the working new voids will form. The specific volume for ductile metals can only be determined with an error of about 1 per cent.

The specific volume of a voidless conglomerate of two kinds of crystallites must be a linear function of the composition. Let x and y represent the masses of both kinds of crystallites, whose specific volumes are v_1 and v_2 , then according to the law of mixtures, the specific volumes of the mixtures of the two crystalline varieties, when brought together without interstices will be, $v = \frac{xv_1 + yv_2}{x + y}$. Substituting $x = x + y - y$ in the above we will have

$$v = v_1 + (v_2 - v_1) \frac{y}{x + y}.$$

Since $\frac{x}{x + y}$ indicates the concentration, it is seen that the volume of a series of conglomerates is a linear function of the concentration.

In a series of conglomerates, which consist of two crystalline varieties, the relation of the specific volume to the concentration, is indicated by a straight line. On the formation of solid solutions, the change in volume, on mixing the components in the anisotropic state, is frequently very small. Hence the specific volume of a series of solid solutions in relation to their composition, as a rule is described by either a straight line or curve, which approaches a straight line. The curves showing the relation of specific volumes to the concentration, then, do not permit us to determine whether the conglomerates consist of solid solutions or of crystallites of pure components. Since the change in volume at the combination of the components into a compound, as a rule is much greater, it is possible to ascertain in this manner the composition of the compounds occurring. Two straight lines will then intersect at the composition of the compound, namely those representing the volumes of two series of conglomerates having the compound as a common component. Although this method for determining the composition of the compound seems to be very simple and rather certain, yet even on careful determination of the specific volumes, it has not given very satisfactory results.

The following are the compositions for which Maey (*Zeitschr. f. phys. Chem.* 29, 119 (1909); 38, 292 (1901)) found breaks on the lines representing the specific volumes of the binary alloys in relation to their compositions. Further, the formulae of the metallic compounds are indicated, whose compositions have been established by thermal analysis and microscopic investigation.

Maey found

SnAg₃
Au₂Pb₂
Au₂Bi₃
BiPb or Bi₂Pb₃
FeSb

Thermal data gave

SnAg₃
Au₂Pb and AuPb₂
Au and Bi form no compounds
Pb and Bi probably form the compound PbBi
Fe₃Sb₂ and FeSb₂

Out of five cases, the determination of the composition of the compounds on the basis of the specific volume has only proven correct once.

With the gold-lead alloys, the conditions of the application of the method are not fulfilled. It assumes that the investigated alloys consist of two crystalline varieties. The gold-rich lead alloys however up to 55 per cent. gold, if they have not been cooled too slowly, consist of four kinds of crystallites, Au, Au₂Pb, AuPb₂ and Pb (Vogel, *Zeitschr. f. anorg. Chem.* 45, 21 (1905)). The method then leads to a false result in this case on account of the abnormal structure of the alloys. In the other cases the basis for the incorrect results is found perhaps in the insufficient accuracy of the determination of the specific volumes.

In the amalgams of sodium and potassium, this method of determining the compounds on the basis of the relation of the specific volumes to the composition has also failed. The formulae of Maey correspond here only partially with the correct formulae.

Maey found:							
NaHg ₃	NaHg ₅	NaHg ₇	NaHg	Na ₂ Hg			
Schüller found (<i>Zeitschr. f. anorg. Chem.</i> 40, 385 (1904)):							
	NaHg ₃	NaHg ₅	Na ₂ Hg ₁₁	NaHg	Na ₂ Hg ₃	Na ₂ Hg ₅	Na ₂ Hg ₇
Maey found:							
KHg ₁₂	KHg ₁₁	KHg ₃	KHg ₅	KHg			
Jaenecke found (<i>Zeitschr. f. anorg. Chem.</i> 58, 249 (1907)):							
	KHg ₃	K ₂ Hg ₅	KHg ₅	KHg ₇	KHg		

It is accordingly only possible in special cases to determine the composition of a compound from the relation of the specific volume to the composition and then only with a knowledge of the equilibrium diagram and the structure of the alloys. The limits of miscibility gaps cannot be determined from this relationship. These questions are however no longer of interest since the equilibrium diagrams of the common metals are known. If we wish to determine the specific volume and density of an alloy series it is only necessary to determine the specific volume of the compounds, the saturated solid solutions and the components, since the specific volume of conglomerates consisting of two constituents may be calculated from the law of mixtures.

2. The Volume and Length Changes of Conglomerates for Variations of Temperature and Pressure.

The thermal dilatation of crystals differs in general in different directions. The same is true for the changes of dimensions of a crystal caused by the action of hydrostatic pressure. Only the crystals belonging to the regular system alter their form for changes of temperatures and pressure in such a way that they retain a form similar to that at the start, while for crystals of the other systems, small variations in symmetry occur. Spheres which are ground from regular crystals, remain as such when subjected to variations in temperature and pressure, while spheres from hexagonal and tetragonal

crystals change into rotation ellipsoids and those from rhombic, monoclinic and triclinic crystals change into triaxial ellipsoids.

Hence it follows, that in a conglomerate, consisting of crystallites of a regular substance no permanent strains appear through variations of temperature and pressure while in conglomerates which are built up of crystallites of non-isometric substances, the strains which already exist, must change. If the conglomerate consists of two kinds of crystallites, which are not isometric and which moreover do not possess similar thermal dilatation and compressibility, the permanent strains must change for the pressure and temperature variations.

The question now arises whether these strains are large and under what circumstances they can reach amounts which will exceed the elastic limit. The answer to this question is of importance for the interpretation of the thermal dilatation and compressibility of conglomerates in relation to their composition.

If a bar consisting of crystallites of the regular system is fixed at the ends and heated, then a pressure p is exerted on the supports due to the thermal expansion. The pressure for the thermal dilatation is $\frac{1}{l} \frac{dl}{dT}$ and the linear compressibility $\frac{1}{l} \frac{dl}{dp}$; if ΔT indicates the rise in temperature this relation becomes:

$$(1) \quad -\frac{\frac{dl}{dT}}{\frac{dl}{dp}} \Delta T = p.$$

If we assume that the thermal dilatation, the linear compressibility and elastic limit are independent of the temperature, then the rise in temperature, which would be necessary to reach p_0 as calculated for copper is 1130° and lead is 500° .

The elastic limit at 0° in a copper or lead bar, with fixed ends would accordingly not be exceeded by heating from 0° up to the temperature of the melting point of the metal. But the elastic limit decreases with increasing temperature and also the thermal dilatation and the compressibility change with the temperature. However since the ratio of the thermal dilatation to the compressibility changes only slightly with increasing temperature and the elastic limit decreases, an exceeding of the elastic limit and therefore permanent deformation of the bars may take place at high temperatures.

Another question is whether strains appear in the interior of the conglomerates of non-isometric crystallites by increasing the temperature or applying hydrostatic pressure. However since the differences of thermal dilatation and of compressibility are slight in different directions, it would then necessitate a considerable change in temperature or pressure in order to increase the strains up to the limit of the strength of the conglomerate or crystallite.

When the conglomerate consists of two different kinds of crystallites, the strains will be able to attain a little larger value. If the above relations for the two crystalline varieties are indicated by the indices 1 and 2, then for a temperature rise ΔT the strain p in respect to the crystalline variety with the smaller elastic limit becomes:

$$(2) \quad -\frac{\frac{dl_1}{dT} - \frac{dl_2}{dT}}{\frac{dl_1}{dp}} \Delta T = p.$$

For a copper-iron alloy the difference in the numerator would amount to $5 \cdot 10^{-6}$, and the linear compressibility of copper, $1 \cdot 10^{-4}$. A temperature rise of 100° would then produce only a strain of 5 kg. per sq. cm.

The thermal dilatation of conglomerates, that consist of two different crystalline varieties if no internal strains appear in them should be calculated correctly according to the law of mixtures. On account of the internal strains, variations appear which however do not exceed the errors of measurements.

While the thermal dilatation of a series of alloys which consist of two crystalline varieties is approximately a linear function of total concentration, in a series of alloys which consist of solid solutions, the thermal dilatation in relation to the concentration in general is represented by a curve. If the thermal dilatation decreases with increasing additions to a pure metal, the alloys formed deserve special consideration on account of their low thermal expansion.

Guillaume (*Les Applications des Aciers au Nickel*—Gauthiers-Villars, Paris (1904)) investigated the thermal dilatation of nickel steels in relation to their composition and found that the additions of nickel to iron and iron to nickel decrease the thermal dilatation of these metals between 0 and 50° . Fig. 179 shows the relation of the linear expansion $\frac{1}{l} \frac{dl}{dT} \cdot 10^6$ to the composition of the alloys.

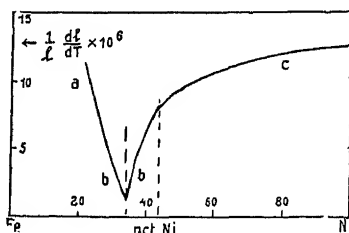


FIG. 179

Nickel steel with 36 per cent. nickel has a vanishing small thermal dilatation. "Invar" an alloy of this percentage is used in the manufacture of scales, pendulums, etc. The alloys with 43 per cent. nickel

have the same thermal dilatation as glass and are used as substitutes for platinum wire which was formerly used exclusively for sealing into glass vessels, e.g. incandescent lamps.

According to the equilibrium diagram of nickel steels, Fig. 165, p. 255, at ordinary temperatures, they consist of two series of solid solutions whose boundary lies at about 36 per cent. nickel. Accordingly the curve for linear expansion (Fig. 179) is seen to consist of two branches, which intersect at 36 per cent. nickel. The curve *ab* indicates the relation of the expansion to the nickel content of the solid solutions with the α -iron space lattice and the curve *cb* the relation to the iron content of the solid solution with the α -nickel space lattice.

3. The Mean Specific Heat of Metallic Compounds in Comparison to the Mean Specific Heat of their Components.

The total heat content of a body can only be ascertained when its specific heat as a function of the temperature is known down to the vicinity of the absolute zero. The integral $\int_0^T c_p dT$ where c_p indicates the specific heat at constant pressure and T the absolute temperature, will give the total heat content of a unit weight of a body at the temperature T . This heat content differs from the energy content by quite a large amount, which does not change with temperature and pressure. This energy is the source of the heat of combination.

Naturally we compare the change of heat content of different bodies for similar temperature intervals, or what amounts to the same thing, their mean specific heats for similar temperature intervals. In this manner, C. Neumann and H. Kopp calculated the mean specific heats of chemical compounds (oxides and salts) from the mean specific heats of their components according to the law of mixtures and compared them with the observed mean specific heats. They found that the mean specific heat of compounds is made up additively of that of their components; this also applies to the changes of heat content in the corresponding temperature interval.

In order to determine the specific heat of a series of alloys which consist of two crystalline varieties, the knowledge of the specific heats of these two crystalline varieties is sufficient as the value of the specific heats of these alloys lie in a straight line, which connects the values of the specific heats of both crystalline varieties. If the specific heats of metallic compounds are additive of those of their components, then the specific heats of metallic compounds also lie on a straight line which connects the values of the specific heats of their components. Therefore for the entire series of alloys, if solid solutions are not considered, a single straight line will establish the relation of the specific heats of all alloys of two components to their composition. However if the specific heats of the metallic compounds

are not accurately additive, two lines will intersect at the composition of the compounds, which represent the specific heats of the two series of alloys consisting of two crystalline varieties.

To test the Neumann-Kopp law, H. Schimpff (*Zeitschr. f. phys. Chem.* 71, 288 (1910)) and P. Schübel (*Zeitschr. f. anorg. Chem.* 87, 81 (1914)) have carried out the determination of the specific heats of metallic compounds and their components between -190° and 600° . The results of these measurements are compiled in the following tables.

Tables 33 and 34 contain the true atomic heat of the metals, that is, the true specific heat c_p , multiplied by the atomic weight of the metal, for the temperatures indicated in the tables. Table 35 compiles the differences in per cent. between the observed molecular heat of the compound c_p of the compound multiplied by the molecular weight—the sum of the atomic heats of the components of the compounds.

TABLE 33
TRUE ATOMIC HEATS OF METALS, ACCORDING TO SCHIMPF

	-150°	-100°	-50°	0°	50°
Mg	4.30	4.93	5.43	5.79	6.02
Al	3.71	4.54	5.19	5.63	5.89
Si	2.31	3.21	3.95	4.54	4.96
Cr	3.12	4.13	4.90	5.44	5.74
Ni	3.86	4.79	5.52	6.06	6.39
Co	3.97	4.77	5.39	5.83	6.08
Sb	4.95	5.39	5.72	5.94	6.05
Au	5.25	5.54	5.78	5.97	6.10
Pb	5.77	5.85	5.97	6.14	6.37
Bi	5.49	5.67	5.86	6.06	6.27
Cu	4.29	4.98	5.48	5.79	5.90
Zn	4.84	5.32	5.70	5.96	6.11
Ag	4.97	5.46	5.80	6.01	6.06
Sn	5.36	5.75	6.09	6.38	6.59

TABLE 34
TRUE ATOMIC HEATS OF METALS, ACCORDING TO SCHÜBEL

	50°	100°	200°	300°	400°	500°	600°
Mg	5.99	6.15	6.40	6.66	6.86	7.03	—
Al	5.84	6.04	6.34	6.56	6.70	6.87	—
Cr	5.63	6.05	6.25	6.30	6.50	6.99	7.81
Fe	—	6.43	7.00	7.49	7.86	8.25	—
Ni	6.34	6.65	7.26	7.75	7.30	7.37	7.40
Co	6.09	6.34	6.73	7.08	7.60	8.14	—
Cu	5.88	5.98	6.14	6.32	6.45	6.63	6.87
Zn	6.10	6.26	6.52	6.65	6.74	—	—
Ag	6.03	6.08	6.14	6.25	6.43	6.70	7.07
Sn	6.59	6.80	7.44	—	—	—	—
Sb	6.01	6.12	6.29	6.46	6.68	7.12	—
Pb	6.33	6.50	6.87	7.08	—	—	—
Bi	6.18	6.32	6.59	—	—	—	—

TABLE 35

DIFFERENCES BETWEEN THE TRUE MOLECULAR HEATS OBTAINED AND THE CALCULATED VALUES IN PER CENT., ACCORDING TO SCHIMPF AND SCHÜBEL

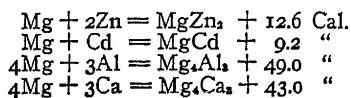
	-150°	-100°	0°	100°	200°	300°	400°	500°
Cu ₂ Mg	-0.5	-1.1	-1.4	-0.9	-0.2	0.8	4.7	—
Cu ₂ Al	-1.8	-2.1	-1.7	-0.7	-0.1	-0.4	0.8	2.6
CuAl	-5.3	-4.4	-2.8	-1.2	-1.0	-0.5	1.3	—
CuAl ₂	-0.1	0.1	-0.1	-0.4	-0.8	-1.2	-1.2	-2.2
Cu ₂ Sb	9.1	6.3	4.2	5.3	5.3	5.2	6.4	—
Cu ₂ Sb	6.4	4.2	2.6	3.9	4.0	4.4	—	—
AgMg	-5.5	-4.7	-3.7	-1.7	-0.6	-0.2	-0.2	-0.4
Ag ₂ Al	2.5	0	-1.3	1.2	2.6	3.3	3.4	1.7
Ag ₂ Al	0.9	0	0.3	1.8	2.4	2.7	3.2	4.0
Ag ₂ Sb	3.1	3.1	2.3	2.0	3.1	10.9	—	—
MgZn ₂	-1.9	-1.9	-1.9	-1.9	-1.5	0.4	—	—
MgNi ₂	—	-2.3	-6.2	-4.9	-6.1	-8.9	-3.5	-3.6
Co ₂ Sn	2.0	0.9	0.4	0.4	—	—	—	—
Ni ₂ Sn	1.8	-2.0	5.7	-7.8	—	—	—	—

For half of the investigated metallic compounds, the variations from Neumann-Kopp law are less than the maximum possible error by 2 per cent. For the other half the variations exceed the error of determinations, the average difference being 4 per cent.

The heat capacity of the Mg-compounds is somewhat less than that calculated, and their heats of formation are especially large. However the evolution of heat is not small on the formation of the Sb-compounds and yet the observed specific heat is greater than that calculated. Even the position of the melting points of the compounds in comparison to those of their components cannot be correlated with the variations from the Neumann-Kopp law. Hence although this law does not always hold accurately, yet the deviations from it are of little importance. Therefore it follows that the heat of combination arises almost entirely from the portion of energy content, which is present in the substance, when $T = 0$.

4. The Heat of Formation and Heat of Fusion of Metallic Compounds.

The heat of solution of the uncombined metals in hydrochloric acid minus the heat of solution of the metallic compound gives their heat of formation. In this manner, W. Biltz and Hohorst (*Zeitschr. f. anorg. Chem.* 121, 1 (1922)) determined the heat of formation of the following metallic compounds in kg.-cal. per mole.



The heat of fusion of the metallic compounds can be determined either calorimetrically or from the duration of the arrests according to the manner indicated on page 42. G. D. Roos (*Zeitschr. f. anorg. Chem.* 94, 329 (1915)) ascertained the following values:

	Heat of Fusion in gm.-cal. per gm.	Heat of Combination gm.-cal. per gm.
CaZn_{10}	77.0	290
CuAl_2	76.5	270
CaZn_4	83.5	184
MgZn_2	65.8	160
MgCd	9.6	130
Cu_2Cd_3	26.1	115
NaCd_2	22.8	115
NaCd_5	16.9	100
NaHg_2	14.7	42

In general the heat of fusion increases with the heat of combination.

5. The Color of Alloys.

The majority of metals reflect the components of white light in almost the same intensity and hence appear white, or for a lower intensity of the reflected light, gray. For copper the intensity of the reflected red light is considerably greater than that of the other colors, whence the copper appears red, and for gold the intensity of the yellow light is greater upon reflection than the other colors. Since the light reflected from copper and gold has beside the red and yellow a quite considerable quantity of all colors, the red and yellow lights will be mixed with white. For the white and gray metals the reflected white light hinders the recognition of the specific colors of the metals, as yellow for nickel and blue for zinc. There are two methods for the definite recognition of the specific color of a metal.

1. Through numerous reflections by the same metal the specific color is affected relatively less than the others. The specific color appears clearer with the number of the reflections. If two polished strips of the investigated metal are fastened on two black strips, whose ends are hinged together and the distances regulated by a screw, a light ray which enters through a hole in the one of the strips and passes out through another can be reflected many times. Through subjective observation by the use of clouded light or through illumination with an arc light and the projection of the image of the emerging ray on a screen, the specific colors of the metals can be easily recognized.

2. The observation of a polished piece of metal with a nicol is simpler, but the specific colors are not so clearly brought out as by many reflections. If we look through a nicol at a suitable angle at a polished surface of metal and turn the nicol around on its axis, then a deepening of the properties of the metal takes place when

the long diagonal of the rhombic cross section of the nicol is absolutely perpendicular to the plane of incidence; if the nicol is turned from this position then the color is faded considerably.

It is an old experience that through sufficient addition of gray metals, the specific colors of copper and gold are suppressed. The production of a gray color occurs in the solid solution series of copper and nickel at 23 per cent. nickel and with manganese at 22 per cent. manganese, accordingly at $\frac{1}{4}$ mole nickel or manganese. How-

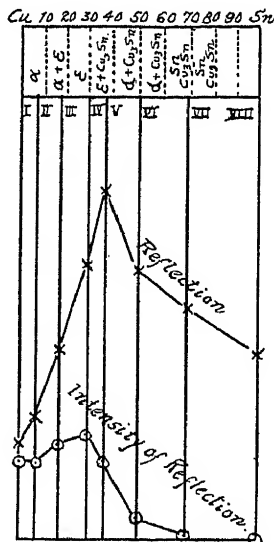


FIG. 180

ever the color change does not occur suddenly but gradually and the characteristic color of copper may be observed by the above methods at higher contents of the added metal. The tendency to produce a gray color in copper is very different for different metals. For example, 20% Pd = 0.13 mole Pd, 40% Pt = 0.18 mole Pt, 19% Al = 0.35 mole Al and 50% Zn = 0.50 mole Zn, color copper gray after first giving yellow and yellow gray colors.

Gold also loses its color by the addition of other metals that form solid solutions with it. If in gold-silver alloys the gold content falls below 65 per cent., they are a greenish yellow and if it falls below 30 per cent., they are white. By the addition of 5 per cent. tin or 4 per cent. bismuth the gold is colored gray.

Concerning the color of copper-tin alloys, M. Chikashige (*Zeitschr. f. anorg. Chem.* 124, 335 (1922)) has made comprehensive investigations. He photographed the spectrum of the original white light and

that of the light twice reflected from the alloy and determined the length of the spectrum in relation to the tin content (curve of reflection in Fig. 180) also the time for the same blackening in the red was determined (intensity of reflection). The constituent Cu_3Sn reflects practically white light, copper practically only red, and tin from red to blue. The light reflected from Cu_3Sn is very white and more intense than that from the copper-rich solid solutions which are used for mirrors, since they are harder and give better sections than Cu_3Sn .

6. The Magnetic Properties of Binary Alloys.

Substances are divided into three groups according to their ability to affect the lines of force of a magnetic field: ferromagnetic substances which possess the ability to concentrate lines of force to a great degree, the paramagnetic which possess this ability weakly and the diamagnetic which weakly disperse the lines of force. The ferromagnetism is then only a stronger paramagnetism; a very strong diamagnetism, that is, a negative ferromagnetism is unknown.

The para- and diamagnetism, the effect of substances on magnetic lines of force is a property which the bodies do not lose by change of their state of aggregation, but which only changes discontinuously when the transition into another state of aggregation takes place at constant temperature. Hence paramagnetism can increase, decrease or even pass over into diamagnetism. Ferromagnetism is on the other hand associated entirely with a definite crystalline form. All ferromagnetic crystals or crystallites undergo transformation into paramagnetic crystals with the absorption of heat. Ferromagnetism is, however, not associated with a certain high energy content of the molecules or atoms. In fact the absorption of heat which accompanies the disappearance of ferromagnetic properties, is very small.

(a) **Ferromagnetism.** The alloys of the three ferromagnetic elements, iron, cobalt and nickel with each other are all ferromagnetic. A portion of the iron-nickel alloys, from 27 to 35 per cent. nickel are barely magnetic at room temperature. However, upon cooling to -100° a strong ferromagnetism occurs in them, which disappears on heating to about 400° . The alloys of iron, cobalt and nickel with non-ferromagnetic metals are only markedly magnetic above a certain content of ferromagnetic metals.

Ferromagnetism is, however, not only characteristic of metals of the iron group, but there are, as Heusler found, even alloys of non-ferromagnetic metals, which are distinguished through high magnetic susceptibility.

1. The relation of ferromagnetism to the composition of the alloys of ferromagnetic metals (Fe, Co, Ni) with non-ferromagnetic metals.

The following rule applies to the ferromagnetism of the alloys of iron, cobalt and nickel with non-ferromagnetic elements. The series of solid solutions which the ferromagnetic metal forms with the non-ferromagnetic metal and in which the ferromagnetic metal in a certain

sense is regarded as solvent are ferromagnetic. Since the solid solution saturated with non-ferromagnetic metal is accordingly ferromagnetic, so are the alloys, which contain it as a constituent. The second constituent may be the compound highest in ferromagnetic metal or the saturated solid solution of this compound and the ferromagnetic metal. In this case the ferromagnetism decreases in the mass according to the amount of ferromagnetic solid solution present. The strong magnetic susceptibility as a rule vanishes at the composition which corresponds to the particular compound or its saturated solid solution in ferromagnetic metals. Rather small variations in the compositions of alloys, whose total composition lies very near the compound highest in the ferromagnetic metals or saturated solid solutions, can be perceived with the aid of the compass since small amounts of saturated ferromagnetic solid solution affect the compass considerably.

The compounds of ferromagnetic metals with other metals as a rule are not ferromagnetic, on the other hand the compounds of iron, cobalt and nickel with elements of metalloidal nature, especially the compounds richest in the ferromagnetic metals are ferromagnetic.

FeO , Fe_3O_4 , Fe_2O_3 , FeS are known to be ferromagnetic; also Fe_3P and Fe_2P , as well as Fe_3C are magnetic, and Fe_3Sb_2 is also slightly ferromagnetic. For the oxides, sulphides, phosphides of cobalt and nickel according to the present unreliable data—their metal-rich compounds are not known for certain—the appearance or disappearance of the ferromagnetism seems to alternate. Co_4S_3 and Ni_3S_2 are magnetic while FeS_2 , NiO and NiS do not appear to be ferromagnetic. It is very striking that the compounds with high heat of formation, as the oxide of iron and FeS exhibit the ferromagnetism of iron, while the compounds with much lower heat of formation do not show it.

The following table gives the formulæ of the compounds of iron, cobalt and nickel with non-ferromagnetic elements where the equilibrium diagrams have been established:

TABLE 36

	Fe	Co	Ni
Si	FeSi	Co_2Si , Co_3Si_2 , CoSi	Ni_2Si , Ni_3Si , Ni_4Si
		CoSi_2 , CoSi_3	NiSi , Ni_2Si_3 ?
Sn	Fe_3Sn_7 ?	Co_2Sn , CoSn	Ni_3Sn_2 , Ni_3Sn , Ni_4Sn
Al	FeAl	CoAl , Co_2Al_3 , Co_3Al_2	NiAl , NiAl_2 , NiAl
Sb	FeSb_2 , Fe_3Sb_2	CoSb , CoSb_2	Ni_4Sb_3 , NiSb , Ni_3Sb_2 , Ni_4Sb
Bi	No compound	No compound	NiBi , NiBi_3
Mg	—	—	Ni_2Mg , NiMg_2
Zn	FeZn_7 , FeZn_3	CoZn_4	NiZn_3 , NiZn ?

Copper, silver, gold and lead form no compounds with the ferromagnetic metals. The compounds Fe_3Sn_7 , Ni_4Sn , Ni_4Sb and FeZn_3 are, however, hard to produce free from the saturated solid solutions rich in the ferromagnetic metal, therefore their slight magnetic susceptibility is perhaps due to the small amounts of these solid solutions.

Only Ni_2Mg and Fe_3Sb_2 of the compounds of ferromagnetic metals (Table 36) are perceptibly magnetic. It may be stated that ferromagnetism is destroyed by the process of chemical combination and only in isolated cases a perceptible ferromagnetism remains. The relatively strong ferromagnetism of the oxides, of the iron phosphides and iron sulphides is therefore worthy of note.

For solid solutions in whose formation ferromagnetic metals participate, the law holds that solid solutions of a ferromagnetic solvent are magnetizable while those of a non-magnetic solvent are not magnetizable. Table 37 gives this information in more detail. The limits of the series of solid solutions are given in per cent. by weight of the ferromagnetic metals; the sign + is added to the indicated series of solid solutions if ferromagnetic and the sign — if non-ferromagnetic.

With the copper-rich solid solutions of iron and cobalt, a question-mark is found in place of the expected minus sign, because it is not certain whether this effect on the compass is produced by free iron or cobalt or by their solid solutions.

The observation "in part" at the Cu-Ni, Co-Cr and Cr-Ni alloys designates that at room temperature only a part of the series of solid solutions is magnetizable. At lower temperature, however, a portion of the solid solutions lower in ferromagnetic metals become magnetizable.

TABLE 37

MAGNETIC PROPERTIES OF SOLID SOLUTIONS OF FERROMAGNETIC METALS

	% Fe	% Co	% Ni
Cu	100-99 + 0-2.5?	100-90 + 0-4 ?	100- 0 + in part
Ag	No solid solutions	No solid solutions	100-96 +
Au	100-82 + 0-20 —	100-96.5 + 0-5.5 ?	100-90 ? + 5? - 0 ?
Si	100-80 +	100-92.5 + 9- 0 —	100-94 + 86-81 —
Sn	100-81 +	100-97.5 +	100-85 +
Pb	No solid solutions	No solid solutions	100-96 +
Al	100-66 + 48-40 —	100-90.5 + 80-68 —	100-85 + 79-68.4 —
Tl	No solid solutions	No solid solutions	100-98 +
Sb	100-95 ? 46-41 ?	100-87.5 +	100-92.5 + 55-54 — 40-33 —
Bi	No solid solutions	No solid solutions	100-99.5 +
Cr	Pseudoternary	100-0 + in part	100-43 + in part 42- 0 —
Zn	100-80 + 0-0.7 —	—	100-54 ? 14-23 ?

The laws concerning the magnetic properties of the compounds and solid solutions of ferromagnetic metals give us at once the magnetic properties of the whole alloy series if the equilibrium diagram of the two metals is known, and on the formation of the alloys all reactions are completed. It is only necessary to bear in mind that the magnetic susceptibility extends from the ferromagnetic metal up to the nearest compound or its saturated solid solution in the ferromagnetic metal. All other alloys are non-magnetizable. If the ferromagnetic metal forms no compound with the other component then all alloys up to the non-magnetic metals are magnetizable or perhaps only up to the saturated solid solutions in the non-magnetic metals at the experimental temperature.

For the accurate determination of the magnetic intensity \mathfrak{I} of a ferromagnetic material its field must be homogeneous, which would only be the case if it took the form of an ellipsoid and was homogeneous in the interior. For the conglomerates consisting of solid solutions, the latter condition is not accurately met, since the orientations of the crystallites are not the same. This condition is fulfilled even less in conglomerates, which consist of crystallites of a saturated ferromagnetic solid solution and of a paramagnetic crystalline variety. The amount of ferromagnetism depends here on the form of the conglomerate and its structure. This agrees with the fact that the magnetization of mixtures of two powders of ferromagnetic and paramagnetic material decreases more rapidly with diminishing amounts of ferromagnetic material, than would be expected from the proportion present. The curves of the magnetic properties in relation to the composition are accordingly equivocal. The curves vary considerably from the expected lines if the alloys consist of two constituents and if a series of solid solutions is formed the deviations are at once very great. A solid solution can even be more magnetic than the ferromagnetic metal contained in it. The magnetization of a cobalt-chromium alloy with 15 per cent. chromium exceeds that of cobalt by about $1/3$.

2. The effect of foreign metals on the temperature of the loss of magnetic properties.

The three ferromagnetic metals lose their magnetic properties on exceeding definite temperatures. It has been shown for iron by the investigations of Seebeck, Mauritius, Gore, Pionchon, Osmond, Le Chatelier, Svedelius, Charpy and Guernet, Roberts-Austen and P. Curie that at the transformation of α - into β -iron, a discontinuous drop of magnetic properties occurs, and that again a small discontinuous change of magnetic properties appeared at the transformation of the β - into γ -iron. These discontinuous changes of magnetic properties are accompanied by small changes in heat content and volume. An addition of carbon displaces the temperature of these changes of properties and changes their character, because it influences the transformation of the iron; hence the changes of magnetic properties remain associated with the corresponding changes of state. Even for nickel the discontinuous

change of magnetic properties is accompanied by a discontinuous change of heat content, which, however, is unusually low for the expected change in volume. For cobalt, data are lacking concerning the changes of heat content and volume at the temperature of the discontinuous change of its magnetic properties. However, from the effect of foreign metals on the transformation temperature of ferromagnetic metals and especially from the indications of this effect on the structure of the alloys, it is quite certain that quite generally the loss of the magnetic properties is associated with the transformation of the magnetic into a heteromorphous non-magnetic crystalline variety.

An influence on the transformation temperature of the α -forms of the iron, cobalt and nickel is then to be expected only when other metals have dissolved in the γ - or β -crystals. This influence consists of a widening of the transformation temperature to an interval, and in that the beginning and the end of the interval is moved towards the transformation temperature of the pure ferromagnetic metals. Metals which at higher temperatures are insoluble in the stable non-magnetic form of the ferromagnetic metals may have no effect on the temperature of the loss of magnetic properties of the ferromagnetic metals in their alloys. Silver, thallium, lead which are insoluble in crystallized iron of the various forms do not influence the temperature of the loss of magnetic properties. The same is true for silver, thallium, lead and bismuth in relation to cobalt. With nickel, miscibility was found throughout for the investigated metals.

However, when solid solutions do form in some cases, the transformation temperature is practically independent if the concentration of non-magnetic additions, as in the following table in which the concentration interval of the solid solution is indicated.

Silicon influences only slightly the temperature of the loss of magnetic properties of the iron, but increases it for nickel considerably and decreases it for cobalt.

TABLE 38.

	Fe	Co	Ni
Au	Without influence 100-72% Fe	Without influence 100-96.5% Co	Without influence 100-90% Ni
Ag	Without influence No solid solutions	Without influence No solid solutions	Without influence 100-96% Ni
Sn	Without influence 100-81% Fe	Influences 100-97.5% Co	Influences 100-85% Ni
Sb	—	Influences 100-87.5% Co	Without influence 100-92.5% Ni

As a rule a foreign substance dissolved in the crystal of ferromagnetic metals will lower its transformation temperature, however, an increase of the transformation temperature appears in two cases. Four per cent. lead raises the transformation temperature of nickel

about 5 per cent., and an addition of 10 atomic per cent. of silicon raises the transformation temperature of nickel up to about 600°. Also the metals which ordinarily lower the transformation temperature of ferromagnetic metals may sometimes show an extraordinarily high value, e.g. the effect of chromium on the transformation points of cobalt and nickel. The effect of foreign metals on the transformation temperature of the three ferromagnetic metals is accordingly quite different. Very large increases or decreases occur if seldom and on the other hand no perceptible influence may be noted.

Van't Hoff (*Rapports présentés au Congrès international de Physique*, Paris, II, p. 532) has stated that when (1) the ferromagnetic metals separate in the pure state at the transformation temperature and (2), the work of the separation of pure ferromagnetic metals from the solid solutions at the transformation temperature can be calculated according to the law of osmotic pressure, the influence of foreign metals on the transformation temperatures of ferromagnetic metals can be calculated like the depression of the freezing point according to the formula

$$\Delta T = \frac{m}{M} \frac{0.02 T^2}{L}$$

Here M indicates the molecular weight of the dissolved metals and m the dissolved amount in grams in 100 grams of the ferromagnetic metals. Values of $\frac{\Delta T M}{m}$ which are smaller than the value $\frac{0.02 T^2}{L}$ can be attributed to the fact that at the transformation no ferromagnetic metal separates but a solid solution. The value calculated with the aid of the heat of transformation L must then not be smaller than the largest value found in order to agree with Van't Hoff's second assumption.

Table 39 gives the depression of the transformation temperatures ΔT , for solid solutions of the content m in 100 grams of ferromagnetic metals and the value $\frac{\Delta T}{m}$. M , where M indicates the atomic weight of the dissolved metal. The molecular depression for solid solutions was calculated for small contents of the non-ferromagnetic metal as far as possible. If we calculate the value of $\frac{0.02 T^2}{L}$ for the transformation of nickel, where $T = 625^\circ$ and $L = 0.013$ cal. per gram (M. Werner, *Zeitschr. f. anorg. Chem.* 83, 275 (1913)) then as maximum depression of the transformation point per 1 gram-mole. of a metal forming solid solutions with nickel in 100 grams of nickel, we get a value of 6000. The depressions found, even those of bismuth and chromium, are considerably smaller than this value.

At an earlier date, Pionchon and Hill (*Verhandl. d. d. physik. Ges.* 4, 194-203 (1902)) gave the heat of transformation for nickel as 4.5

cal. per gram, which is too large. This gives a value of 1700 for $\frac{0.02T^2}{L}$, which is smaller than the values found for bismuth and chromium.

TABLE 39

DEPRESSION OF THE TEMPERATURE OF THE LOSS OF MAGNETIC PROPERTIES THROUGH THE SOLUTION OF FOREIGN METALS IN THE MAGNETIZABLE METALS

Metal Added	Fe			Co			Ni		
	m	Δt	$\frac{\Delta TM}{m}$	m	Δt	$\frac{\Delta TM}{m}$	m	Δt	$\frac{\Delta TM}{m}$
Cu	2.5	27	700	5.2	30	360	12.0	25	130
Ag	0	0	—	0	0	—	4	0	0
Au	to 28	0	0	—	—	—	10	0	0
Si	5.2	10	54	4.4	52	320	5.2	-570	-3000
Sn	to 19	0	0	2.5	129	6000	5.2	22	510
Pb	0	0	—	0	0	—	2	-5	-400
Al	11.1	25	62	8.0	70	240	5.2	180	1100
Tl	0	0	—	0	0	—	2.1	13	1200
Sb	—	—	—	13.6	209	1850	8.0	0	0
Bi	0	0	—	0	0	—	1	20	4000
Cr	—	—	—	11.1	370	1720	2	180	2400

The influence of the composition of series of alloys on the temperature of the loss of magnetic properties can be easily seen from the equilibrium diagram. The transformation points of pure metals in the solid solutions of ferromagnetic metals as a rule are influenced by the additions. The temperature at which the magnetizable α -form vanishes completely, rises or falls up to the end members of the series of saturated solid solutions and does not change by further additions. Then a second non-magnetic crystalline variety appears together with the saturated solid solution. Hence all alloys from the saturated solid solution in the ferromagnetic solvent up to the concentration of the next alloy of homogeneous structure (compounds or saturated solid solutions) have the same temperature of the disappearance of the magnetizable form.

(b) Paramagnetism. The magnetization of mixtures of para- or diamagnetic material depends neither on their form nor on their inner structure, because here the mutual effect of the magnetized crystallites on each other may be disregarded. Therefore the magnetic susceptibility χ will be a linear function of the amount of the individual crystalline varieties, of which the alloy is composed. These straight lines intersect at the composition of pure compounds and those of saturated solid solutions. The diagram (Fig. 181) gives the results of K. Honda (*Am. J. Phys.* 32, 1003 (1910)) for the changes of χ in the alloys of nickel with aluminum. The alloys with less than 80 per cent, nickel no longer contain saturated nickel-rich solid solu-

tions and are hence weakly magnetic, i.e. paramagnetic. In a series of alloys consisting of two crystalline varieties, χ changes linearly and these straight lines intersect at the composition of the compound. The structure of the alloys is likewise indicated in Fig. 181 and it will be noted that it is in good agreement with the relation of χ to the composition.

At 550° the nickel-rich solid solutions are no longer ferromagnetic, but paramagnetic. The curve (b), Fig. 181, shows the relation of their

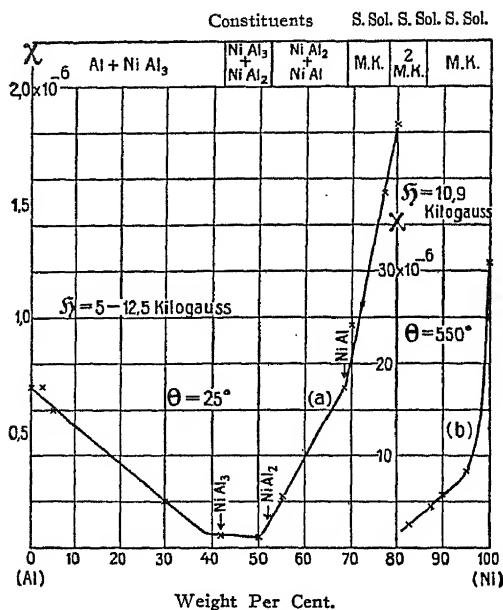


FIG. 181

χ value to the concentration. The paramagnetism of the solid solution at 550° is much greater than that of the alloys with less than 80 per cent. nickel. Although the compounds NiAl_3 and NiAl_2 contain considerable amounts of ferromagnetic metals, their susceptibility is considerably smaller than that of aluminum.

For the alloys of nickel and tin, K. Honda found a very similar satisfactory conformity between the χ values and the structure of the alloys.

For the zinc-copper alloys, R. H. Weber (*Ann. d. Phys.* 62, 671 (1910)) found that the diamagnetic susceptibility had a pronounced maximum in the vicinity of 32.7 per cent. copper. In the γ -solid solution series, χ increases rapidly with decreasing copper content and diminishes just as rapidly with decreasing amounts of the zinc-rich γ -solid solution.

(c) The Heusler alloys. Heusler discovered strong magnetic properties in manganese alloys which contained no ferromagnetic metals. Additions of aluminum, tin, arsenic, antimony and bismuth to manganese-copper, containing 30 per cent. manganese, produced considerable ferromagnetism. There is a considerable amount of literature to be found regarding these alloys. Heusler and Richarz (*Zeitschr. f. anorg. Chem.* 51, 265 (1909)) have made an extensive study of these alloys.

According to Hindrichs (*Zeitschr. f. anorg. Chem.* 59, 478 (1908)) manganese and aluminum form two compounds, Mn_3Al and $MnAl_3$.

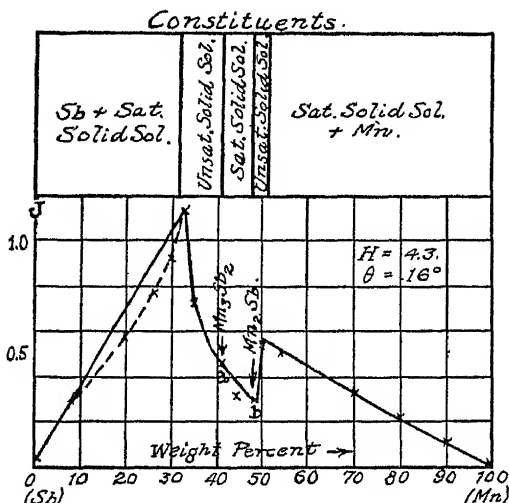


FIG. 182

The compound Mn_3Al is very weakly ferromagnetic. Through the addition of copper to this compound the ferromagnetism increases considerably. It has not been determined whether the copper forms solid solutions with the Mn_3Al or a ternary compound.

The manganese-antimony alloys have also been investigated as to their structure and magnetic properties. Honda (*Ann. d. Phys.* 32, 1019 (1910)) obtained the lines as shown in Fig. 182, for the relation of magnetic intensity to the composition of the ferromagnetic alloys at 16° . The maximum of J does not correspond to the compound Mn_3Sb_2 , but rather to a saturated solid solution of this compound with 8 per cent. antimony, which corresponds very closely to the compound $MnSb$. Consequently it must not be assumed that a maximum or minimum intensity will always occur at the composition of the compound, although the maximum of J in the series of solid solutions of cobalt-chromium seems to indicate this. (Lewkonja, *Zeitschr. f. anorg.*

Chem. 59, 326 (1908).) Perhaps the magnetic properties of these alloys are closely related to the crystalline varieties Mn_3Sb and Mn_2Sb which they contain and the solid solutions formed from them. However, the two pure components are slightly less magnetic than the antimony-rich solid solution of the compound Mn_3Sb_2 and the manganese-rich solid solution of the compound Mn_2Sb .

As with all of the Heusler alloys, the manganese-antimony alloys also lose their ferromagnetism upon heating. The two compounds should lose it in a discontinuous manner at a definite temperature; however, according to Honda's determinations this is not the case, Fig. 183.

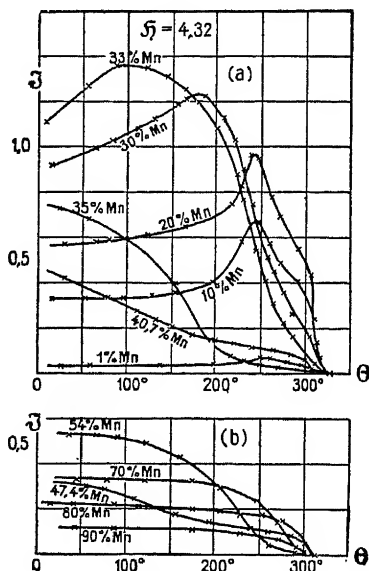


FIG. 183

Above 320° all manganese-antimony alloys are paramagnetic. Even the magnetic susceptibility χ of these alloys at 550° is according to Honda, very closely connected with their structure, and changes linearly with the composition for the alloys consisting of two crystalline varieties (Fig. 184).

7. The Relation of Hardness and Flow Pressure to the Composition in a Series of Solid Solutions.

Kurnakow and Žemčužny (*Zeitschr. f. anorg. Chem.* 54, 149 (1907); 60, 1 (1908); 64 (1909); Kurnakow u. Puschin, 68, 123 (1910); Kurnakow u. Smirnow, 72, 31 (1911)) have shown that the hardness and flow pressure always increase through isomorphic admix-

ture of the one substance with another so that the hardness and flow pressure of a series of solid solutions have maxima for the central compositions of continuous series of solid solutions. This rule seems to be general for metallic and non-metallic solid solutions.

Its basis is to be sought in a general relation of the molecules of the two substances to each other. This relation may be formulated that the forces of the attraction of two different molecules are always greater than the force of attraction of two similar molecules in the same mixture (G. Tammann, *Über die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen*, L. Voss, Leipzig (1907), p. 35).

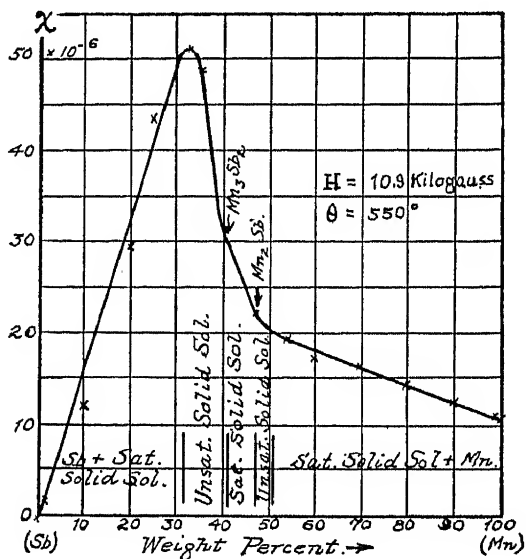


FIG. 184

Consequently the internal pressure, which is determined by the sum of the forces of attraction per unit of surface increases in a liquid upon the addition of a second substance and will have a maximum for equal concentrations of the two substances.

The hardness and flow pressure are properties which are not proportional to the internal pressure, but increase or decrease with it. From the law of Kurnakow and Žemčuzny, it follows that the internal pressure in a series of solid solutions has a maximum; from this it follows that even in the anisotropic state the attraction of two unlike molecules is greater than that of two similar molecules as is well known in the isotropic state.

When the two alloying substances form no compounds, then the maximum of the internal pressure must exist at a mixture of the

same number of molecules of the two substances. When they form a compound, the concentration of the maximum is displaced.

The hardness of metallic compounds is greater than that of either component. A summary of these data has been made by Kurnakow and Žemčuzny (*Zeitschr. f. anorg. Chem.* 60, 35). For the compounds in which non-metallic substances enter, it often happens that the compound is softer than either of its components. Thus the hardness of Molybdenite, MoS_2 , is about 1.2 according to Moh's scale, while that of sulphur is 2 and that of molybdenum is 8.5.

Kurnakow and Žemčuzny have determined the hardness either with a sclerometer, in which they drew a steel pin under a constant load across a polished surface of the specimen, assuming that the hardness was inversely proportional to the width of the scratch, or they determined the Brinell hardness.

In the following series of solid solutions they found very distinctly marked maxima of hardness for equal atomic-concentration of solid solutions: Cu-Ni, Au-Ag, Au-Cu, CaSiO_3 - MnSiO_3 (maximum between 15 and 30 per cent. CaSiO_3). Moreover, they determined the pressure at which the flow from the cylindrical tube of the conglomerates of a series of solid solutions reached a constant rate of extrusion. For the solid solutions of AgCl and AgBr, KBr and KI, p-dichlorobenzol and p-dibromobenzol, stearic acid and palmitic acid, indium and lead as well as thallium and lead, very distinctly marked maxima of flow pressure were found at equal molecular concentrations.

8. The Pressure at which the First Slip Lines Form and the Brinell Hardness.

Determinations of both properties for the manganese-copper alloys are given below. The Brinell hardness, BH, has been determined by Guillet (*Étude industr. des alliages*, p. 757 (1908)) and Wologdin (*Revue de Metallurgie* (1907), 36) and the pressure uE , at which slip planes form in the mixed crystallites of the manganese-copper alloys, by Tammann (*Zeitschr. f. phys. Chem.* 80, 687 (1911)). Both pressures in kg./sq. cm. are given in the following table, together with the ratio BH/uE .

TABLE 40
COPPER-MANGANESE ALLOYS

Mn. per cent. by weight	0	10	20	30	40	50
BH	5,000	7,200	7,600	13,000	14,600	18,700
uE	203	220	243	290	330	342
BH/uE	24.6	32.5	31.3	44.8	44.2	54.7

The pressure of Brinell hardness exceeds only that of the elastic limit, at which the first slip planes form, but also the pressure required to cause a cube to begin to flow when acted upon from two

opposite sides. This pressure for copper amounts to 2780 kg./sq. cm., while the Brinell hardness is 5000 kg./sq. cm. Since a large portion of the pressure for a Brinell test is distributed laterally and the material moreover is greatly strengthened by the deformation, this result is easily understood.

The ability of a metal for glide-surface formation is not destroyed by additions, which dissolve in the crystallites of the metal, even if the necessary force for producing the first slip planes increases with increasing additions. In consequence the alloys which consist of solid solutions are workable. The crystallites of metallic compounds are, however, brittle at ordinary temperatures, obviously because the ability for formation of slip planes is lacking. Hence no alloy which contains a metallic compound is workable at ordinary temperatures.

9. The Electrical Conductivity of Binary Alloys.

The resistance r of a metallic cylinder is directly proportional to its length l and inversely to its cross section q .

$$r = \rho \frac{l}{q}.$$

Let $l = 1$ cm. and $q = 1$ sq. cm. then $r = \rho$. The resistance of a symmetrical cube, whose edges are each 1 cm., to a current is called the specific resistance of the metal and its reciprocal value, the specific conductance. Since the conductivity is determined by the volume of the conductor, then the composition in per cent. by volume will express the relation of the conductivity to the composition of the bodies. The conductivities or resistances of similar volumes for the different amounts of the metals A and B are accordingly compared.

(a) The relation of conductivity to the composition. Matthiessen (*Pogg. Ann.* 103, 428 (1858); 110, 190, 222 (1860)) on the basis of numerous measurements divided alloys into two groups according to the relation of the conductivities of alloys to their composition by volume. For the alloys of one group, this relation is almost linear, as for the alloys: Sn-Zn, Sn-Sb, Sn-Cd, Pb-Cd and Zn-Cd. For those of the other group, the conductivity of the pure metals is decreased considerably by additions. The curve, which gives this relation for the entire series of alloys of two such metals, is like a catenary curve, which is not like the ordinary curve, in which the chain is equally loaded between two fixed points, the conductivity values of the two pure metals, but like a chain whose load decreases as it proceeds from the fixed points. This form of the relation of conductivity to the composition appears for example in the alloys, Au-Ag, Au-Cu, Cu-Ni, and Co-Ni.

Le Chatelier (*Revue générale des Sciences* 6, 531 (1895)) assumed that the linear relation held, when the alloy consisted of the crystallites of the two pure metals and that the strong depression of the conductivity was caused by the existence of solid solutions.

Since then the knowledge of the equilibrium diagrams of alloys has been enlarged considerably, Guertler (*Zeitsch. f. anorg. Chem.* 51, 397 (1906)) and Kurnakow (*Ber. d. Polytechn. Ist., St. Petersburg*, 6, 569 (1906) and *Zeitschr. f. anorg. Chem.* 54, 149 (1907)) with their collaborators have confirmed these suppositions. Kurnakow especially,

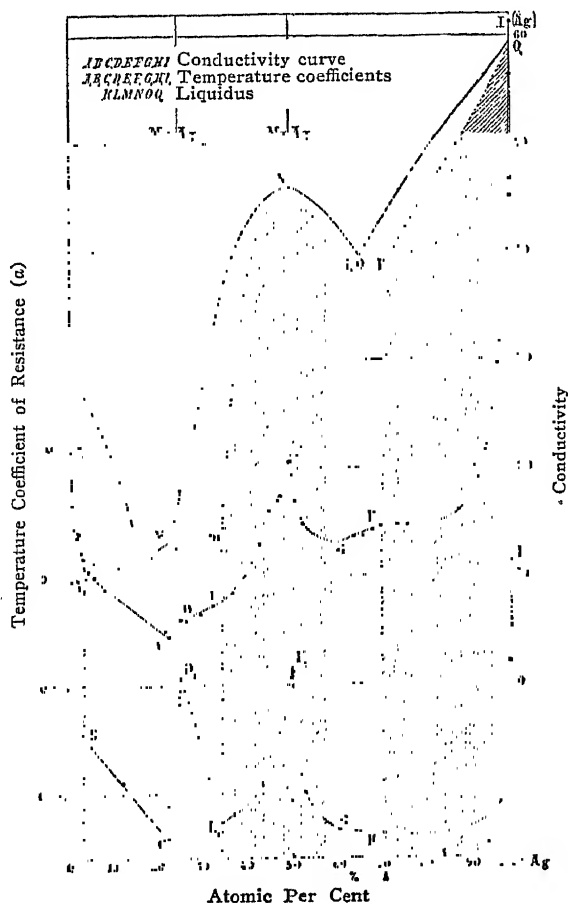


FIG. 185

has extended the knowledge in this field by experimental investigations and also explained the connection of the electrical conductivity to the elastic properties of the alloys. Benedicks (*Recherches sur l'acier au carbone*, Upsala (1904) and *Zeitschr. f. phys. Chem.* 40, 545 (1902)) concluded at an earlier date that equal molecular amounts

of different metals dissolved in α -iron increased its resistance by equal amounts and that they effected the hardness of iron in a similar manner.

In general the relation of the conductivity to the volume-concentration of a component can be described by two rules.

For the alloys which consist of two crystalline varieties the conductivity changes approximately linearly with the volume concentration, and for alloys which consist of one crystalline variety it changes on a curve, decreasing rapidly at first and then slowly with increasing concentration of the one component as it proceeds further from the other pure component. In this respect the metallic compounds act similarly to the components.

It is only necessary to know the value of the conductivity of the components, of the compounds and of the saturated solid solutions, to construct the dotted lines, which give the relation of the conductivity to the composition of the entire series of alloys.

In Fig. 185, the lines A B C D E F G H I give the relation of the electrical conductivity of the Mg-Ag alloys to the composition (Smirnow u. Kurnakow, *Zeitschr. f. anorg. Chem.* 72, 31 (1911)). The line K L M N O Q represents the temperature of the beginning of crystallization. In the shaded fields, each alloy consists of one crystalline variety and in the unshaded, of two crystalline varieties. Inside of the shaded field the conductivity changes on curves, which slope sharply from the values of the components Ag and Mg and of the compound Mg_3Ag ; and inside of the unshaded portion, this change takes place almost on a straight line. The crystals of the compound Mg_3Ag dissolve no Ag, but do dissolve about 2.5 atomic-per cent. of Mg. A perceptible lowering of conductivity appears due to the formation of solid solutions.

If, however, the equilibrium diagram of the Mg-Ag alloys had not been known previous to the investigation of the relation of conductivity it would have been possible to have easily overlooked the compound Mg_3Ag on the basis of this relation. Even the determination of the relation of the conductivity to the concentration of the alloy would not be suitable for ascertaining the composition of the saturated solid solution P_2 , since the conductivity in the vicinity of its composition changes but slightly or not at all with the concentration. It would be still more difficult to determine in this manner the composition of the saturated solid solution m (Point E), because the break at E is very slightly marked.

A general method for determining the constitution of the alloys cannot accordingly be based on the concentration-relation of the conductivity, but when the constitution of the alloys is known the number of conductivity determinations may be lessened considerably. In general it is sufficient to carry out the determinations for the compounds and the saturated solid solutions.

In these determinations, especially with the brittle alloys—the metallic

compounds without exception are not ductile—many difficulties have to be overcome. If the material cannot be drawn into a wire, it can be made into the form of small rods by melting in either porcelain or glass tubes (Stepanow, *Zeitschr. f. anorg. Chem.* 78, 1 (1912)). In this manner the magnesium-silver alloys were made since only the alloys from 0 to 7 atomic-per cent. of magnesium could be drawn into wire.

Fig. 186 (Guertler, *Zeitschr. f. anorg. Chem.* 51, 401 (1906)) shows the almost linear relation of the conductivity of several alloys of cad-

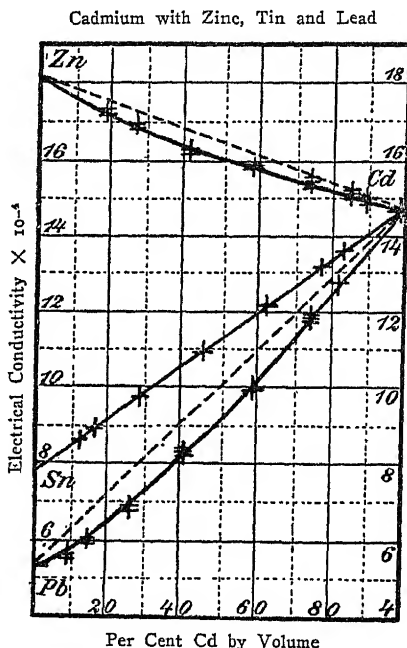


FIG. 186

mium according to the measurements by Matthiessen. It will be noticed that the tin-cadmium alloys follow a straight line most closely. At 122° the compound CdSn_4 (?) forms from the crystallizing alloys consisting of almost pure cadmium and the solid solution rich in tin with about 2 per cent. cadmium. The existence of this compound is not indicated by the relation of the conductivity to the composition.

The type of curve for complete miscibility in the crystalline state is shown in Fig. 187 (Guertler, *Zeitschr. f. anorg. Chem.* 51, 401 (1906)).

The linear relation expected between the conductivity and composition cannot always be confirmed for the alloys consisting of two crystalline varieties. Stepanow has found very perceptible variations

from the linear relation for the magnesium-rich alloys of tin, lead, zinc and bismuth, which consist of pure magnesium and of a compound of the mentioned metals. The conductivity of magnesium decreases unusually rapidly for small additions of the mentioned metals so that it would be assumed that the magnesium forms solid solutions with them. According to the investigations of Grube (*Zeitschr. f. anorg. Chem.* 44, 117 (1905); 46, 76 (1905); 49, 72 (1906)) this is not the case. It seems here that it is caused either by gaps between the crystallites or by the products of the action of magnesium-rich melts on the melting pot.

From these deviations it is very evident how little we may conclude

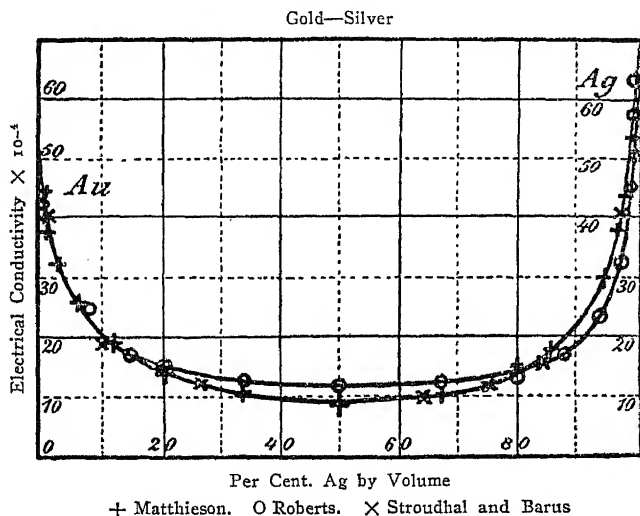


FIG. 187

concerning the structure of an alloy from the conductivity of alloys. Only when the equilibrium diagram is established on the basis of thermal and microscopic investigations can the lines of conductivity lead to a confirmation of the general rules, or in case variations appear, to a closer investigation of the causes of these variations. However, it is entirely inadmissible to assert the existence of compounds or series of solid solutions on the basis of the conductivity curves alone.

The metals with high melting points as a rule form with other metals a series of solid solutions rich in the high melting metal. Accordingly it may be assumed that the addition of a foreign metal to a high melting metal will depress perceptibly its conductivity.

In fact the conductivity of iron (Barret, Brown and Hadfield, *Journ. Inst. Elect. Eng.* 31, 674 (1902)) is decreased considerably through small additions of gold, tin, cobalt, nickel, manganese, aluminum, car-

bon and an addition of iron, manganese, copper, silver, gold, iridium, palladium and rhodium to platinum lowers the conductivity of platinum for the same reason (Barus, *Sill. Amer. Journ. Science* (3), 36, 427 (1888); Dewar and Fleming, *Phil. Mag.* (5), 36, 27 (1893)).

(b) The influence of temperature on the conductivity in relation to the composition of the alloys. Matthiessen (*Pogg. Ann.* 112, 353 (1861); 122, 19 (1864)) discovered on the basis of his determinations of the conductivity of alloys at 0° and 100°, a simple law concerning the relation of the temperature-coefficient to the composition.

If ρ_{100} indicates the specific resistance at 100° and ρ_0 that at 0°, also κ_{100} and κ_0 the corresponding values of the conductivities, then,

$$\frac{\rho_{100} - \rho_0}{\rho_{100}} = \frac{\kappa_0 - \kappa_{100}}{\kappa_0} = \frac{P}{100}$$

P then is the per cent. increase of conductivity for the decrease in temperature from 100° to 0°.

If the conductivity κ_m for an alloy is calculated according to the rule of mixtures for volume per cent. of the components and in a like manner its changes with the temperature P_m , indicating further the actual values found by κ and P, then according to Matthiessen:

$$\frac{P}{P_m} = \frac{\kappa}{\kappa_m} = \frac{\rho}{\rho_m}$$

This equation in general is valid whether the alloy consists of one or two constituents.

The pure metals and their compounds (Stepanow, *Zeitschr. f. anorg. Chem.* 78, 30 (1912)) have almost the same value for P, about 29.

For alloys which consist of two crystalline varieties, $\frac{\kappa}{\kappa_m} = 1$ and $P = P_m$. If these two constituents consist of pure metals or their compounds P is almost equal to 29. If on the other hand a solid solution exists in the alloy the value of P is considerably smaller.

The resistance of an alloy consisting of solid solutions can be expressed as the sum of two terms; of a resistance, which is calculated from the resistances of both pure metals according to the rule of mixtures, and of an additive resistance, which expresses the effect of the formation of solid solutions. It is now possible to show that if this law of Matthiessen is valid this additive resistance is independent of the temperature.

The law of Matthiessen in general has been confirmed, but still for certain alloys consisting of solid solutions, a negative value of P occurs, while the law only anticipates a positive. The limitations of the law have not as yet been determined for high and low temperatures.

In Fig. 185, p. 294, the line A B C D E F G H I indicates the relation of the values found for P (temperature coefficient between

25° and 100°) to the composition. This line proceeds quite similarly to the line which indicates the relation of the conductivity of the composition in the magnesium-silver alloys. If this is known, then P

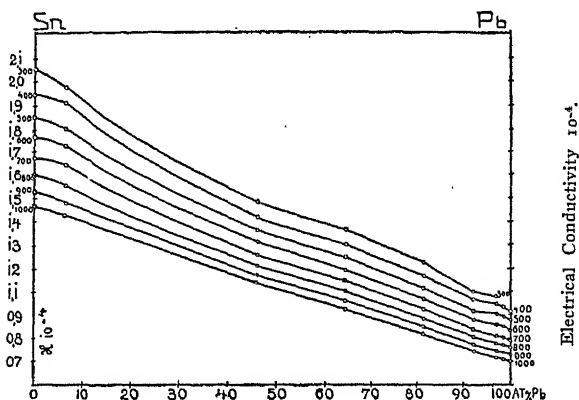


FIG. 188

can be calculated from Matthiessen's law. It will, however, be recognized again that a general method for the differentiation of series of alloys with one or two crystalline varieties cannot be based on the rela-

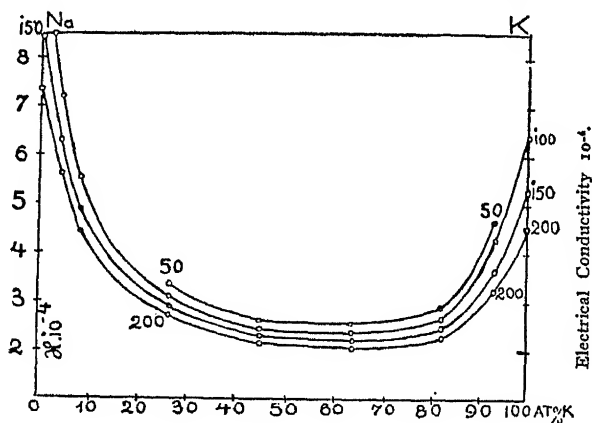


FIG. 189

tion of the value P to the composition. If it were not known on the basis of thermal and microscopic investigation of the alloys, that the alloys between the points G and H, consisted of the two saturated

solid solutions, P_1 and P_2 , then it could be assumed on the basis of the temperature-coefficient curves that the compound $MgAg$ formed a continuous series of solid solutions with silver.

The specific resistance for the alloys consisting of solid solutions is large, its change with the temperature, however, is small. In consequence these alloys have found application in the production of resistance wire, as constantan, copper 60 per cent. and nickel 40 per cent. and manganin, copper 84 per cent., manganese 12 per cent. and nickel 4 per cent. which have large specific resistances and small temperature coefficients.

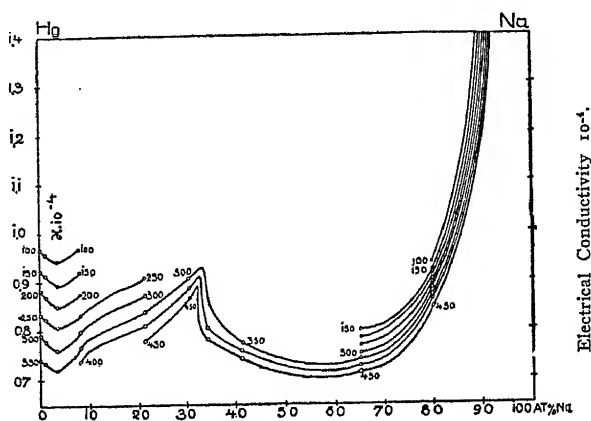


FIG. 190

(c) The conductivity of liquid binary mixtures. K. Bornemann (*Metallurgie* 7, 396 (1910); 9, 473 (1912); *Ferrum* 2, 276 (1914)) has made quite extensive investigations with the aid of his collaborators, regarding the relation of the conductivity of liquid alloys to the composition and the temperature.

The relation to composition gives three types of curves: 1. Almost linear, as for the mixtures of tin with lead (Fig. 188). 2. The isotherms of the conductivity resembling a catenary (Fig. 189). 3. Secondary maxima and breaks appearing on the isotherms of the latter type (Fig. 190).

The isotherm of conductivity for potassium-sodium is almost like those of nickel-copper and copper-zinc, while on those of copper-antimony, copper-aluminum and copper-tin, secondary maxima or breaks appear.

The characteristic relation of the conductivity to the composition for the series of solid solutions is likewise found in liquid mixtures, and is thus not a specific characteristic of solid solutions. The variations from the path of a catenary in individual cases is connected with

compounds, which crystallize from the melt; there are, however, compounds which do not appear perceptibly on the conductivity isotherms, as Na_2K and on the other hand there are secondary maxima and minima to which no crystallized compounds correspond.

The relation of conductivity to the composition and that of the temperature coefficient of the resistance are frequently similar. This is true also for liquid alloys.

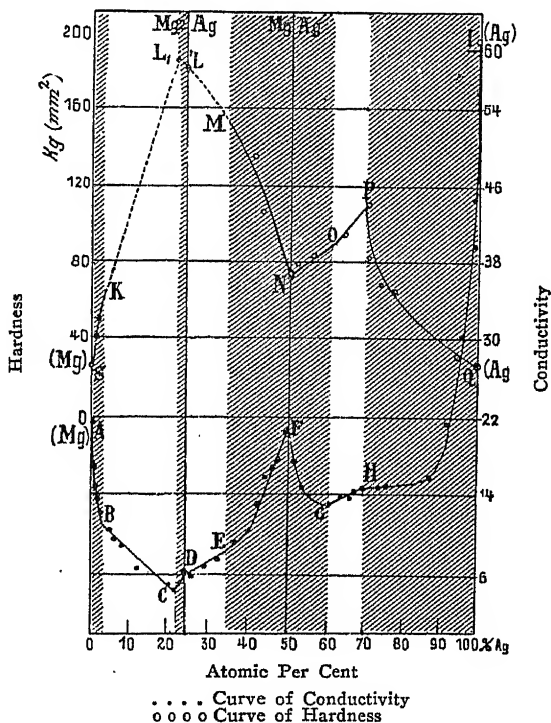


FIG. 191

(d) **Conductivity and hardness.** Kurnakow and his collaborators have investigated the relation to the concentration of electrical conductivity and of hardness, which they determined either by the sclerometer or according to the method of Herz-Brinell (p. 83), and found that the hardness increased as the conductivity decreased by the formation of solid solutions. Also the metallic compounds have as a rule a greater hardness than their components. In Fig. 191, the line S K L₁ L M N O P Q indicates the Brinell number and A B C D E F G H I, the electrical conductivity for the magnesium-silver alloys (Smirnov and Kurnakow, *Zeitschr. f. anorg. Chem.* 72, 31 (1911)). The fields of alloys consisting of one constituent, i.e. of solid solutions, are

shaded, while in the unshaded area the alloys consist of two constituents (Fig. 185). When the hardness of the two constituents does not differ very much, then the Brinell test for the alloy containing equal volumes of the two crystalline varieties, approaches the mean value of hardness of the two crystalline varieties. Naturally the hardness of such a conglomerate is indefinite, since it must change abruptly from one to the other crystallites. The true hardness of both crystalline varieties must be represented by two lines proceeding parallel to the concentration axis.

For the copper-silver alloys it is shown that the hardness of silver increases through the formation of solid solutions with copper and that of copper increases through the formation of solid solutions with silver, while the conductivity decreases (Kurnakow, Puschin and Senkowsky, *Zeitschr. f. anorg. Chem.* 68, 123 (1910)).

For the alloys of softer metals (lead-indium, lead-thallium) the flow pressure can be determined. It appears, that for the lead-indium alloys, which consist of a continuous series of solid solutions, a maximum appears at about 50 atomic-per cent. of indium. For the same concentration the minimum of the conductivity curve appears and that of the curve of its temperature coefficient. Indium is softer than lead and yet the flow pressure of lead is more than doubled by the addition of indium.

W. Geibel (*Zeitschr. f. anorg. Chem.* 69, 38 (1911) and 70, 240 (1911)) showed that the tensile strength of wires of the alloys of palladium and gold, palladium and silver, and of palladium and platinum which consist only of solid solutions had a distinct maximum at 50 atomic-per cent., while the conductivity and temperature-coefficient had their minimum value at about this composition.

In general, not only for metallic bodies, the internal pressure in a crystal and also its tensile strength, flow pressure and hardness seem to increase by the absorption of a foreign substance. With reference to the changes of conductivity the metallic conducting solid solutions must be distinguished from the electrolytic conductance. For metallic conducting crystals the conductivity is impaired through formation of solid solutions, but improves for salts (Benrath, *Zeitschr. f. phys. Chem.* 64, 693 (1909)).

(e) The electrical resistance of ternary alloys. In a series of metallic solid solutions the resistance increases greatly with the first additions of the second metal and then reaches a flat maximum. If by the addition of a third metal to the binary alloy with the maximum resistance there is a further great increase in the resistance, this fact would be of importance in the preparation of resistance wires. The addition of a third metal appears as a rule, however, to cause only a small change of the resistance.

With copper-nickel alloys an addition of 7.4 per cent. manganese causes an increase in resistance that has approximately the same absolute amount for the whole alloy series. An addition of 17 per cent.

chromium to the copper-nickel alloys lessens the resistance of copper-rich alloys and doubles that of the alloy with 20 per cent. copper (Hunter and Bacon, *Trans. Amer. Electrochem. Soc.* 33, 186).

Fig. 192 (K. Fischbeck, *Zeitschr. f. anorg. Chem.* 125, 1 (1922)) gives the course of the curves of the same resistance for a comprehensive investigation of the gold-silver-copper alloys. The curves are the specific resistances in Ohms multiplied by 10^6 . An addition of silver to the copper-gold alloys of maximum resistance increases the resistance only very little and soon decreases it. The surface of resistance of the gold-silver-copper alloys has a weakly defined maxi-

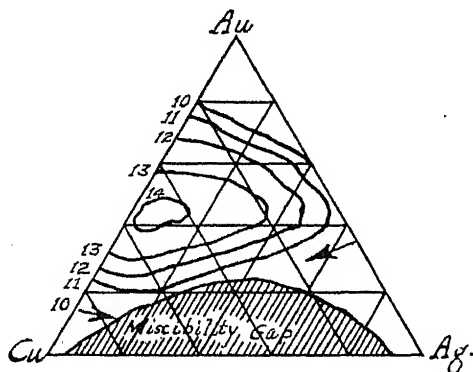


FIG. 192

mum at the composition of 70.5 per cent. gold, 25.2 per cent. copper and 4.3 per cent. silver. The temperature coefficient of resistance is represented by a surface which is a mirror-image of the surface of resistance.

(f) **Heat conductivity.** The heat conductivity λ and the electrical conductivity κ are parallel in a series of metals. λ/κ is a constant which changes only slightly with the nature of the metals (Law of Wiedemann and Franz). Consequently it would be expected, that λ/κ would change only slightly in a series of metallic solid solutions. According to the investigations of F. A. Schultze (*Physik. Zeitschr.* 12, 1028 (1911)) this is approximately the case, still the heat conductivity does not diminish so quickly with increasing amounts of the alloyed metals as the electrical conductivity. The ratio λ/κ has a maximum then at equal concentrations of the component of the solid solution, in which it exceeds the ratio for the two pure metals from 20 to 40 per cent. Schultze determined the ratio λ/κ directly for the alloys of palladium with silver, gold and platinum which form a continuous series of solid solutions.

If a series of alloys of two metals which form a continuous series of solid solutions are made up in the rod form and are arranged parallel to each other at distances corresponding to their content of one

component and then are coated with a layer of wax, and heat applied to the one end of each, the points where the wax just melts will form a curve similar to a catenary.

10. The Thermoelectric Force of Alloys.

A flow of heat at the place of contact of two metals produces an electric charge, conversely an electric current produces heat. Since the potential difference of the two metals for not too large a temperature difference is proportional to the temperature difference, it can be stated that the difference in potential at the place of contact of the two metals is proportional to the amount of heat flowing through it in a unit of time. If one metal is replaced successively by a series of its alloys with another metal, without changing the temperature difference which impels the flow of heat the flow of heat will change and with it the difference in potential since the heat conductivity of the alloys changes with the composition. The thermoelectric forces of the thermoelements of a series of alloys with another metal will accordingly change in proportion to the heat conductivity of the series of alloys. The proportionality factor depends, however, on the nature of the concerned metals.

If in a series of alloys, the thermal conductivity (as the electrical conductivity) be a linear function of the composition in volume per cent.—which is the case, when the series of alloys consist of completely unarranged crystallites of the two pure metals—then the linear relation to the volume per cent. of the alloys will hold also for the differences in potential. If, however, the alloy series consist of solid solutions, then the thermal conductivity in relation to the concentration in per cent. by weight changes along a curve, which is similar to a catenary. A quite similar curve would be expected for the relation of the thermal force, if the thermal force of such a series of alloys is measured against another metal. This expectation is only partly fulfilled. According to Rudolfi (*Zeitschr. f. anorg. Chem.* 67, 65 (1910)) the alloys of zinc and cadmium, consisting of almost pure cadmium and zinc crystallites, show an almost linear relation of their thermal force against copper. In a series of solid solutions of gold-silver and copper-nickel, the relation of the thermal force against copper or nickel was according to Rudolfi, very similar to that of the electrical conductivity; and also to that of the thermal conductivity. In the palladium-gold and palladium-silver alloys, which likewise form continuous series of solid solutions, Geibel (*Zeitschr. f. anorg. Chem.* 69, 38 and 70, 240 (1911)) found a similar relation of thermal forces to the composition of the alloys.

On the other hand, G. Borelius (*Ann. d. Physik.* 53, 615 (1917)) found that the thermal force in relation to the concentration in atomic-per cent. also produced a linear relation as in the series of solid solutions of palladium-platinum and series of solid solutions of nickel-copper.

Considerable variations appear for certain alloys, the thermal forces of

which should be a linear function of the concentration since they consist of two crystalline varieties. Such alloys are those of bismuth and cadmium, antimony and tellurium, also bismuth and tellurium (W. Haken, *Ann. d. Phys.* 32, 291 (1910)).

H. The Chemical and Electrochemical Properties of Binary Alloys

1. The Reaction Limits of Chemical Reagents on Metallic Solid Solutions.

If a homogeneous binary solid solution is subjected to the action of a chemical reagent, it will generally be found that the two components will be attacked unequally. In the cases where the one component is practically unattacked, it will be found that the nobler component exerts a protective influence on the less noble component up to certain limiting values. (*Zeitschr. f. anorg. u. allg. Chem.* 107 (1919) and "Die chemischen und galvanischen Eigenschaften von Mischkristallreihen und ihre Atomverteilung," L. Voss, Leipzig (1919).)

(a) Copper-gold and silver-gold alloys. The reaction limits of chemical reagents on the solid solutions of gold with copper or silver extend only up to definite gold-contents, as 12.5, 25, and 50 atomic per cent. If we consider these gold-contents on the basis of the total number of all atoms in the solid solution as unity (the total number of all atoms in a gram atom is the same) then depending on the nature of the chemical reagent the reaction limit will be $1/8$, $2/8$ and $4/8$ mole gold.

A condition for the appearance of sharp reaction limits is that the two atomic varieties in the space lattice only oscillate around their places in the lattice and do not change their places, accordingly no diffusion takes place in the solid solution. If this condition is not fulfilled, then the reaction limit will extend to a higher gold content with time and especially with increasing temperatures.

At room temperature a weak oxidizing reagent reacts with the copper-gold alloys up to 0.22 mole gold. At 123° the alloys up to 0.55 mole gold show yellow streaks after 2 days, which become orange with time. At 156° the alloy with 0.89 gold even becomes orange after 4 days, while those low in gold show temper colors due to thickening of the oxide layer. At 186° the alloys with 0.96 gold become orange after 2 days and become covered with purple streaks. With increasing temperatures, the effect is moved to still higher gold content, since the copper atoms come to the surface and become oxidized.

The reaction limit of a solution of $(\text{NH}_4)_2\text{S}_2$ at 20° is very sharp and lies at $2/8$ mole gold. At 104° , H_2S reacts distinctly after 3 days even on the alloys with 0.96 gold, which are colored orange.

If the foils of a series of alloys, which have been annealed in a stream of H_2 for a period of 12 hours at 720° are placed in a strong solution of $(NH_4)_2S_2$, then the foils with less than 0.25 mole gold will blacken and the foil richest in gold will remain unchanged even after a period of 4 years. In the following tables, the relative blackening for polished and unpolished foils is indicated. The numeral 0 indicates that the foil was not changed, the numeral 1, that they become entirely black and the decimal value indicates the intermediate effects.

RELATIVE BLACKENING

After	UNPOLISHED FOIL					
	0.230	0.240	0.245	0.255	0.260	0.270 mole Au
1 hour	0.3	0.05	0	0	0	0
1 day	0.8	0.1	0	0	0	0
5 days	0.99	0.2	0	0	0	0
30 days	0.99	0.5	0	0	0	0
80 days	0.99	0.7	0	0	0	0
20 months	1.0	1.0	0.1	0	0	0

After	POLISHED FOIL					
	0.230	0.240	0.245	0.255	0.260	0.270 mole Au
1 hour	0.99	0.7	0.5	0	0	0
1 day	1.0	0.95	0.9	0	0	0
5 days	1.0	0.98	0.95	violet	0	0
30 days	1.0	0.99	0.95	0.2	0.1	0
80 days	1.0	1.0	0.95	0.3	0.2	0
20 months	1.0	1.0	1.0	0.5	0.5	0

The limit for blackening of the unpolished foil lies between 0.245 and 0.255 mole gold; for the polished, it changes with time from 0.245-0.255 to 0.260-0.270 mole gold after 2 to 20 months of exposure.

It is very striking that the limit of blackening of the foil with the natural surface does not lie between 0.245 and 0.255 mole gold after 2 months' exposure, but rather at a less gold content. It appears probable that this was caused by accidental high gold content of the foil. This applies also for pieces from the same rolled strips with 0.245 gold, which differ considerably in the same solution. Several remained unblackened for a longer time while others blackened quickly; the rate of blackening diminished with the concentration of the solution.

If a blackening of the foil with the natural surface takes place with decreasing gold content a thin uniform layer of sulphide is not produced, but spots appear, which indicate copper-rich places.

In this manner the reaction limit was determined for a series of chemical reagents (see Table 41).

For the action of $(NH_4)_2S_2$ on the silver-gold alloys, the blackening takes place up to a gold content of 0.32 mole gold, the normal limit of $2/8$ mole gold here is exceeded and on exposure of the copper-gold alloys to a weak oxidizing reagent, it is not entirely complete. Reagents whose molecules combine with 2 atoms of copper or silver, as

sulphide solutions, weak oxidizing reagents, or solutions of PdCl_2 or PtCl_2 , are effective up to the limit of $2/8$ mole gold.

TABLE 41

Medium; Solutions of	Reaction Limit on Cu-Au Solid Solutions	Reaction Limit on Ag-Au Solid Solutions
PdCl_2	0.245-0.255 mole Au	
$\text{Pd}(\text{NO}_3)_2$		0.245-0.255 mole Au
PtCl_2	0.245-0.255 " "	0.245-0.255 " "
$(\text{NH}_4)_2\text{S}_2$	0.245-0.255 " "	>0.32 " "
Na_2S_2		0.27 -0.32 " "
Na_2S	0.22 " "	0.27 " "
Sulphur in CS_2	0.22 " "	
Na_2Se_3	0.245-0.255 " "	>0.27 " "
Picric acid	0.22 " "	
Alcoholic solution of Sodium Tartrate	0.22 " "	
AuCl_3		0.495-0.505 " "
H_2CrO_4		0.492 " "
HMnO_4		0.495-0.505 " "
HNO_3		0.480-0.490 " "
HgCl	None	
HgNO_3	None	
HgCl_2	Mercury precipitates 0.24 mole Au	
$\text{Hg}(\text{NO}_3)_2$		
Silver salts	0.08-0.15 " "	

The reagents, which only require one atom of copper or silver, as a solution of AuCl_3 , which also contains AuCl , and the strong oxidizing reagents, are effective up to the limit of 0.5 mole gold. The reaction limit of silver salts on the copper-gold alloys is irregular; it occurs at $1/8$ mole gold. In conclusion, mercury is precipitated from its salts by all copper-gold alloys, even by those of 99 per cent. gold; only pure gold will produce no precipitation. This abnormal behavior is caused by the circumstance that the copper-atoms of the surface precipitate mercury and since it combines with the gold, gaps are produced in the lattice structure, whereby the copper-atoms lying lower down come into action.

(b) The series of solid solutions of iron-silicon. Solutions of the following salts: CuSO_4 , $\text{Hg}(\text{CN})_2$, AuCl_3 , PbCl_2 , SbCl_3 , SnCl_2 , FeCl_3 , I_2 and $(\text{NH}_4)_2\text{MoO}_4$, act on the iron-silicon solid solutions up to 0.25 mole silicon (0.241 to 0.261 Si). The solutions of strong oxidizing reagents: chromic acid, permanganic acid and picric acid do not react up to this limit.

The solutions of HCl , H_2SO_4 , Ag_2SO_4 and HgCl_2 act on the solid solution of the entire series from 0.0 to 0.33 mole silicon. The solutions of the nitrates, AgNO_3 , $\text{Cu}(\text{NO}_3)_2$, $\text{Hg}(\text{NO}_3)_2$ and HgNO_3 produce passivity of the iron.

It is quite astonishing that the solid solutions with more than 0.25 silicon evolve hydrogen from acids and precipitate silver, while they do not precipitate gold, mercury and copper.

(c) The series of solid solutions of iron-vanadium. Since vanadium occurs in the electromotive series between copper and hydrogen, the iron-rich solid solutions should precipitate the metals which occur between iron and vanadium in the electromotive series while the vanadium-rich solid solutions should not precipitate them. These metals are: tin, antimony, lead, thallium and cadmium. This is true when no secondary reactions are encountered. The reaction limit on the iron-vanadium series occurs at 0.5 mole vanadium (between 0.43 and 0.54 mole vanadium).

(d) The series of manganese-silver. Rolled foil with 0.26 and 0.28 manganese precipitates the dissolved metals from the solutions of Ag_2SO_4 , AgNO_3 , copper-acetate, PbCl_2 , Ti_2SO_4 , CdSO_4 and ZnSO_4 , on the other hand the alloys with 0.22 and 0.24 mole manganese do not precipitate these metals (P. Siebe, (*Zeitschr. f. anorg. u. allg. Chem.* 108, 174 (1919))). Hydrogen is not generated by the alloys with 0.22 and 0.24 manganese, on the other hand a little is generated with the alloys of 0.26 and 0.28 manganese. The action on the hard foil is not appreciably different from that of the soft. The reaction limit occurs at 0.25 ± 0.01 mole manganese or $6/8$ mole silver.

(e) The series of magnesium-silver. The alloys with 0.10 mole magnesium do not precipitate silver from the solutions of its nitrate and sulphate, while those with 0.15 magnesium only slowly and those with 0.20 and 0.28 magnesium more rapidly. The metals which lie between silver and magnesium in the electromotive series are not precipitated by the solid solutions of magnesium-silver with 0.0 to 0.28 mole Mg, but are by the series with 0.38 to 0.65 magnesium.

(f) The series of copper-nickel. (L. Nowack, *Zeitschr. f. anorg. u. allg. Chem.* 113, 1 (1920)). Weak oxidizing reagents, as atmospheric oxygen in caustic soda or alkaline solution of H_2O_2 , react up to the limit 0.25 nickel (0.24 to 0.26 nickel). The action of a solution of K_2S_2 exceeds this limit, its reaction limit occurring between 0.32 and 0.34 mole nickel.

(g) The series of copper-palladium. The reaction limits of several reagents on the hard and soft alloys of copper-palladium are as follows (L. Nowack, *Zeitschr. f. anorg. u. allg. Chem.* 113, 19 (1920)). The reaction limits lie between the indicated mole fractions of palladium.

Reaction Limit on the Copper-Palladium Alloys

Solution of	Hard	Soft
K_2S_2	0.20-0.22	0.20-0.22 Pd
$(\text{NH}_4)_2\text{S}_2$	0.20-0.22	0.20-0.28 "
KOH or NaOH		0.22-0.28 "
Picric acid		0.22-0.28 "
PdCl_2	0.22-0.28	
Ag_2SO_4	0.20-0.22	0.22-0.28 "
HgNO_3	0.22-0.28	
HgCl_2	0.22-0.28	

2. The Solubility of Hydrogen in the Alloys of Palladium with Gold, Silver and Copper.

The question regarding the state of the hydrogen dissolved in palladium will be discussed at considerable length. On the basis of the relation of the pressure of hydrogen to the concentration of the absorbed hydrogen determined by B. Roozeboom and Hoitsema (*Zeitschr. f. phys. Chem.* 17, 1 (1895)) the following conception of the condition of the dissolved hydrogen can be formed. From the dia-

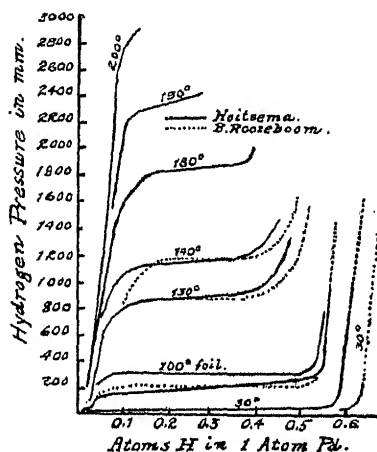


FIG. 193

gram (Fig. 193) for finely divided palladium, it is evident that in a certain concentration interval, the pressure at low temperatures is not independent of the concentration and that it begins to rise in the vicinity of the concentration, 0.5, hydrogen for 1 of palladium. For dense palladium, the pressure at which this rise takes place lies still closer to this hydrogen content. This concentration corresponds to the formation of an easily dissociated compound Pd_2H , the amount of which decreases rapidly with increasing temperatures. The formation of two saturated palladium-hydrogen solid solutions, whose compositions change rapidly with the temperature and whose concentrations are represented by the two strongly curved lines, is improbable on account of the curvature of these lines and on account of the distinct rise of the curves between these two sections. Also no proof that the dense palladium consists of two crystalline varieties is advanced.

The old opinion, that the Pd_2H acted quite similarly to the salt hydrates has been disproven through this diagram. Further Hoitsema has shown that the pressure for small hydrogen-concentrations increases proportionally to the square of the concentration, from which it fol-

lows that the hydrogen moves here as atoms in the palladium, while for the second great increase in pressure, the pressure increases almost proportionally to the concentration, the hydrogen then moves between the molecules of the Pd_2H as molecules.

In the state of saturation below 100° , 1 atom of hydrogen is combined with 2 atoms of palladium. The hydrogen then appears here as bivalent, if it is not desired to assume that alternate palladium atoms are attached to a hydrogen atom.

For the absorption of hydrogen up to the limit of saturation, the palladium absorbs 860 times its volume and increases but 2 per cent. in volume. The lattice parameter consequently changes very little.

A. J. Berry (*Journ. Chem. Soc.* 99, I, 463 (1911)) used a palladium-gold alloy as a cathode in one of two voltmeters filled with sulphuric acid and a platinum cathode in the other, both voltmeters being connected in series in the same circuit. Two anodes of platinum were used. The difference of the two volumes of hydrogen generated gave the amount of hydrogen absorbed by the alloy cathode. In the following table the gold contents of the palladium-gold alloys and the volume of hydrogen, reduced to 0° and 760 mm. absorbed in 1 gram of the alloy are given. The investigation was conducted at room temperature.

Per Cent. Gold	Mole Gold	c.c. of H_2
0.0.....	0.0	73.5
18.5.....	0.109	49.0
33.0.....	0.210	31.5
42.2.....	0.280	22.5
58.9.....	0.437	9.0
63.5.....	0.485	4.5

Additions of gold up to 0.2 mole lower the solubility of hydrogen a little more than the subsequent additions which lower the solubility proportionally to the mole fraction. Judging from linear extrapolation the solubility of the hydrogen at a gold content of 0.52 mole would become zero. Since by electrolytic charging of the palladium with hydrogen according to Thoma (*Zeitschr. f. phys. Chem.* 3, 69 (1889)) supersaturation is ordinarily produced, which disappears slowly, then the solubilities determined by Berry could be a little large. The limit of solubility could thereby approach the gold content of 0.5 mole still closer. Since Berry did not mention that the limit of the hydrogen solubility occurred close to a simple mole fraction, consequently his measurements are not influenced through a preconceived idea concerning the solubility.

Further determinations of the solubility of hydrogen in palladium-gold alloys between the temperatures 223° and 827° were conducted by A. Sieverts (*Zeitschr. f. anorg. u. allg. Chem.* 92, 329 (1915)) and his collaborators, E. Jurisch and A. Metz. Since in this temperature interval, considerable motion of the atoms occurs for the solid solutions of palladium-gold, the solubility of hydrogen even above 0.5 mole

gold (65 per cent. Au) must be perceptible (see p. 325). Fig. 194 gives the isotherms determined for the solubility of hydrogen in the palladium-gold alloys.

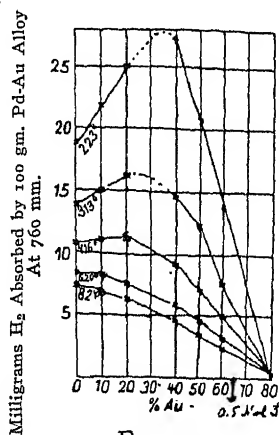


FIG. 194

The solubility of hydrogen in the palladium-gold alloys according to Sieverts and Metz is shown in Fig. 195. A mole fraction of 0.5

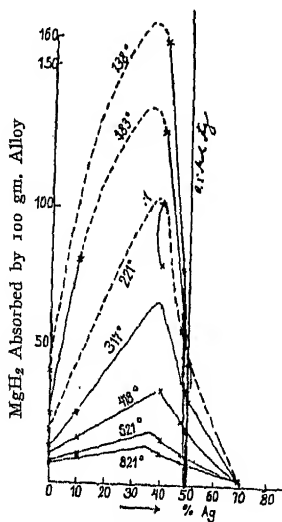


FIG. 195

silver corresponds to 49.7 per cent. silver. It will be seen that at temperatures above 200°, the solubility in the alloys with more than 50 per cent. silver is considerable, while below 200° the solubility in

the alloys with 50 per cent. silver is not perceptible. Sieverts emphasized the fact that at 183° the alloy of 50 per cent. silver is entirely inactive towards hydrogen, while those with 47.4 per cent. silver at 138° will absorb it with considerable rapidity.

At temperatures below 138° , at 100° and 10° , the maximum according to Nowack (*Zeitschr. f. anorg. u. allg. Chem.* 113, 19 (1920)) is again less pronounced and the solubility of the hydrogen becomes zero, if at 100° the palladium content of 0.506 mole and at 15° 0.503 mole are exceeded. The relation for the copper-palladium alloys occurring at 15° to 100° is similar to that of the gold-palladium alloys. The solubility of the hydrogen in the copper-palladium solid solutions at 15° becomes zero at 0.485 palladium and also at 100° becomes zero at 0.500 palladium.

3. The Electrochemical Behavior of the Alloys of Gold with Copper or Silver.

If a solution of CuSO_4 is electrolyzed using two copper electrodes, no oxygen will be liberated at the anode. If a copper-gold alloy is substituted for the copper anode, then for the alloys from 1.0 to 0.284 mole gold, equal volumes of oxygen will be liberated for equal currents and equal time and for the alloys from 0.26 to 0 mole gold, no gas will be liberated. For the silver-gold alloys this limit is displaced to a greater gold content and lies between 0.354 and 0.402 mole gold. (*Zeitschr. f. anorg. u. allg. Chem.* 112, 223 (1920)).

The current-potential curves for a solution of CuSO_4 between a copper cathode and a copper-gold alloy anode, are similar for 1.0 to 0.30 gold, the decomposition voltage lies between 1.40 and 1.50 volts. With decreasing gold content, the decomposition voltage decreases. On the current-potential curve of the alloy with 0.28 gold, there are two decomposition voltages; the first acceleration of the current intensity lies at 0.80 volts; the second at about 1.3 volts. This alloy acts similarly to gold at higher current density and at lower densities it approaches the series with decreasing decomposition voltage. Oxygen is liberated from these anodes of 1.0 to 0.28 gold, which is in agreement with the fact that their current-potential curves are identical with those of the gold.

The same parallelism occurs for the evolution of oxygen and the curves of the potential for the anodes of the silver-gold alloys.

The limits of the evolution of oxygen and decomposition voltages differ essentially in the following ways. If the gold-copper alloys are connected with a copper anode in a solution of a copper salt, and the voltage determined for which a stronger and more lasting polarization current occurs, it will be found that this voltage amounts to 1.40 volts for 1.0 to 0.5 mole gold and then decreases with diminishing gold content. The same will be found for the silver-gold alloys, only here the invariable voltage between 1.0 and 0.5 mole gold amounts to 0.73

volts. These results are shown for the copper-gold alloys in Fig. 196. Line 1 shows the voltage of the beginning of the counter current. Line 2 shows the volume of oxygen evolved for equal current intensity, which becomes zero for the copper-rich alloys. Line 3 indicates the decomposition voltage and line 4, the voltage at which the evolution of oxygen begins. The process, which causes the counter current, must be differentiated from that which determines the decomposition voltage,

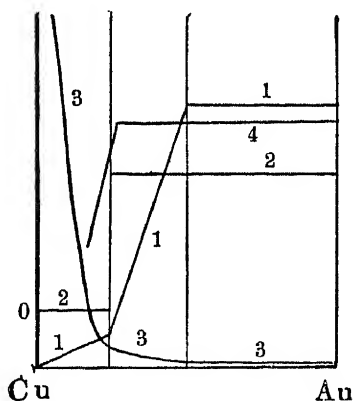


FIG. 196

since the two potentials are dependent in different ways on the gold content of the anodes. (Regarding the basis of this, consult the *Zeitschr. f. anorg. u. allg. Chem.* 112, 233 (1920).)

4. The Parting of Copper-Gold and Silver-Gold Alloys with Nitric Acid.

If a indicates the quotient obtained by dividing the extracted amount of the soluble material by the amount of this material existing in the alloy, then a can vary between 1 and 0. When $a = 1$, the entire original amount of the soluble material is extracted, when $a = 0$, the soluble material is completely protected by the insoluble. The amounts of copper- or silver-, which are extracted by hot nitric acid at 115° from silver-gold or copper-gold alloys are shown by the dotted line in Fig. 197. From the gold content of 1.0 to 0.5 mole gold, the amount extracted from the alloys is not perceptible; from a gold content of 0.50 to 0.375 mole gold, a increases linearly with decreasing gold content and from 0.375 ($3/8$) to 0 mole gold, the entire amount of copper or silver existing in the alloy is dissolved.

The reaction limits do not occur for all reagents in multiples of $1/8$ mole of the inactive metals. The action of some exceeds the limit a little, as in the case of reagents containing sulphur and selenium on

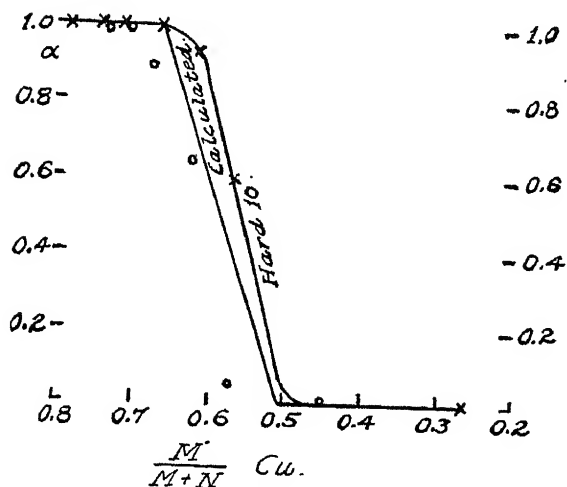


FIG. 197

solid solutions of silver-gold. The action of others like the weak oxidizing reagents on the solid solutions of copper-gold does not quite reach it.

TABLE 42

Components of the Series of Solid Solutions	Parting Limits					
Ag-Au	$\frac{1}{8}$	$\frac{2}{8}$	$\frac{4}{8}$	$\frac{6}{8}$	$\frac{7}{8}$	mole Au
Cu-Au		$\frac{2}{8}$	$\frac{4}{8}$			mole Au
Fe-V		$\frac{2}{8}$	$\frac{4}{8}$			mole V
Fe-Si		$\frac{2}{8}$	$\frac{4}{8}$			mole Si
Mn-Ag	$\frac{2}{8}$	$\frac{2}{8}$	$\frac{4}{8}$	$\frac{6}{8}$	$\frac{7}{8}$	mole Ag
Mg-Ag						mole Ag
Zn-Ag						mole Ag
Zn-Au			$\frac{4}{8}$			mole Au
Pd-Au	$\frac{2}{8}$	$\frac{2}{8}$	$\frac{4}{8}$	$\frac{6}{8}$	$\frac{7}{8}$	mole Pd
Pd-Ag			$\frac{4}{8}$			mole Pd
Pd-Cu			$\frac{4}{8}$			mole Pd

5. The Distribution of Two Kinds of Atoms in the Space Lattice and Their Relation to the Reaction Limits.

When the distribution of two atomic varieties in a space lattice is only controlled by chance, it can be stated on the basis of the theory of probabilities, what fraction of the soluble atomic-variety in the different mixtures is unprotected and in consequence is dissolved. To

this end, the entire mass of atoms is considered as being divided into confines of s -atoms, and examined as to the probabilities of position of protection of soluble atoms existing in these confines. A formula has been obtained (*Chemische und galvanische Eigenschaften von Mischkristallenreihen*, L. Vöss, Leipzig, see p. 12, and *Zeitschr. f. anorg. u. allg. Chem.* 107, 12 (1920)) by which the value of a can be calculated for the various values of s .

$$\Sigma\omega = p^{s-1}q + p^{2s-4}q^2 + p^{3s-7}q^3 \dots\dots\dots,$$

$$a = \frac{q - \Sigma\omega}{q}.$$

$\Sigma\omega$ gives the summation of the probabilities of the protection of the baser atoms by the surrounding nobler atoms for the mole fraction p of the nobler metal, q is the mole fraction of the baser metal and

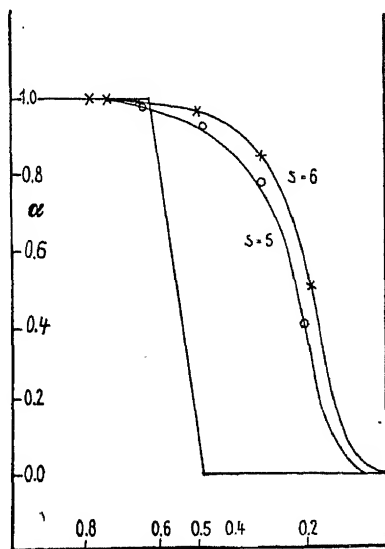


FIG. 198

equals $1 - p$. $s - 1$ is the number of noble atoms, which protect the baser. If this is plotted in relation to the mole fraction, the curves $s = 6$ and $s = 5$, Fig. 198, are obtained. If then a soluble atom is protected by 5 or 4 insoluble atoms then a (the extracted amount divided by the amount of soluble material) varies with the mole fraction in the manner indicated by curves $s = 6$ or $s = 5$. It is seen that the protective effect for the soluble atoms is quite small, that it naturally increases continuously with increasing content of the insoluble com-

ponent, and the protective action decreases slowly, the more insoluble atoms are needed for the protection of one soluble atom.

If the broken lines of the curves of the copper-gold or silver-gold alloys are compared with the curves of extraction, it will be seen that the calculated curves have an entirely different character than those actually found. If the gold and copper atoms were divided according to the theory of probabilities in the space lattice, then a much lower protective action would be expected, as is established for the alloys between 0.5 and 0.7 mole gold, also no sharp reaction limit could appear for a random distribution of atoms in the space lattice. Add to this that the curves of extraction for binary glasses, in which the molecules of the soluble and of the insoluble components are arranged at random, are like those calculated. The question arises what is the regular distribution of two kinds of atoms in the space lattice, and whether this allows an interpretation of the chemical relation of metallic solid solutions.

6. The Regular Distribution of Two Kinds of Atoms in the Space Lattice.

At the separation of a solid solution from its melt, the two kinds of atoms, which in the melt had a twofold random arrangement since their arrangement was completely irregular and their space coördinates were also different, must fit into their space lattice and further must arrange themselves regularly.

If the atoms in the first moment of rapid crystallization do not meet both requirements, but rather distribute themselves irregularly at the points of their lattices, then diffusion occurs in the solid solution at temperatures in the vicinity of the completion of crystallization; the two kinds of atoms are able to exchange their places, whereby all irregularities can be corrected in the regular distribution of atoms. As a result of this atomic motion the regular distribution is distorted in the small areas; these changes in position will, however, be readjusted very quickly. The momentary distribution of the two atomic varieties will accordingly oscillate about the regular. With decreasing temperatures these oscillations decrease in number and finally disappear when the motion of both atomic varieties ceases.

That at the temperatures of our surroundings, the motion of the two atomic varieties practically disappears for solid solutions, whose melting intervals lie at high temperatures, follows from the fact that the reaction limits of such solid solutions are not displaced to higher concentrations of the inactive atomic variety in weeks or years.

Following the cooling of a solid solution, in which the regular distribution of both atomic varieties has taken place at high temperatures, a very regular distribution can continue to exist without any perceptible oscillation. A definition of the regular distribution can be derived in the following manner.

For well-formed crystals of solid solutions it appears that their forms do not differ from those of the crystals of their components. Hence it follows, that the directions of equal value of the properties of the solid solutions in general are the same as those of the pure crystals. Of course there are exceptions. In solid solutions whose components crystallize regularly, double refraction has been observed, and accordingly a variation from the behavior of the pure crystals. Apart from these abnormal solid solutions, the distribution of both atomic varieties on the lattice lines of directions of equal value must be the same, because if variations appear then corresponding variations must be observed also in the properties of directions of equal value.

By the condition of equal distribution on lattice lines of equal value, the distribution of the atoms is not yet clearly determined, because there is a series of distributions, which correspond to these conditions of symmetry. If, however, we add to these conditions, the best possible mixing and bring the mixture into the temperature region of active atomic motion of the two atomic varieties, then their distribution will become definite.

The distribution of two atomic varieties on the lattice lines of each direction must correspond to the ratio of miscibility of the two atomic varieties, because all points of the lattices occupied with atoms lie on the lattice lines. The lattice lines of one direction are joined together into groups by lines with similar distributions or all of the lines of one direction consist of a repetition of groups of lines with similar distributions. The condition of symmetry requires that the groups of lattice lines of the same direction have a similar distribution and the ratio of miscibility of both atomic varieties in a group to correspond to that in the entire lattice.

This requirement resulting from the symmetry of the solid solution can be brought into agreement with that following from the ability of diffusion, because it is required: (1) that aggregations of similar atoms do not occur on the lines. By aggregations are meant a series of two, three, etc., of similar atoms of both atomic varieties, and (2) that the number of lattice lines of a group is a minimum. For two directions which are not of equal value, the number of lattice lines of a group in general are not the same, we are accordingly concerned not with a requirement of an absolute minimum of a number of lattice lines of a group, but rather with a relative minimum, which is consistent with those of other directions, which are not of equal value. In this sense it can be required that the distribution of atoms for a normal solid solution, be such that the number of lattice lines of similar distributions without aggregations in a group in directions of equal value to be equal to each other and the lowest. The number of these lines in the other, likewise directions of equal value must have consistent values.

The distribution of atoms corresponding to this definition is normal. There are still two other kinds of distribution of interest; the distribution, which meets only the condition of symmetry, but not

that corresponding to the best possible mixture and that, which has a good mixing but a lower symmetry than required by the kind of lattice.

The stability relations of solid solutions with these three kinds of distribution can be expressed as follows. Those with normal distribution are the most stable, because in the normal distribution only temporary local changes take place by diffusion. For the distribution with symmetry lower than the lattice, the tendency of transformation to the normal exists and becomes perceptible at higher temperatures. The probability of the formation of distribution, which at imperfect mixing corresponds completely to the condition of symmetry, is even lower at lower temperatures, than on crystallization from solutions. Optically, solid solutions with such distributions would not be differentiated from the normal; at increased temperatures they will transform themselves into the normal solid solutions.

7. The Normal Distribution in a 14-Point Lattice.

Investigation of several metals with X-rays of short wave length has shown that the atoms of Cu, Ag and Au are arranged at the points of the same lattice. The unit of this kind of lattice is a cube that has atoms at its corners and in the centers of its faces. Since this unit has 14 atoms the entire lattice is called the 14-point lattice, abbreviated $(14 \text{ Pg})_a$, where a designates the length of the sides of the cube. Two kinds of lattices are closely related to this lattice. The unit of one is a cube with atoms in the corners, this lattice is the $(8 \text{ Pg})_a$. The unit of the second is a cube with atoms in the corners and an atom in the center, this lattice is the $(9 \text{ Pg})_a$. Both lattices are partial lattices of the $(14 \text{ Pg})_a$. Through interpenetration of the partial lattices the total lattice results. If we have one of the partial lattices with one kind of atom and the other partial lattice with another kind of atom the distribution is the normal one for a certain mixing ratio.

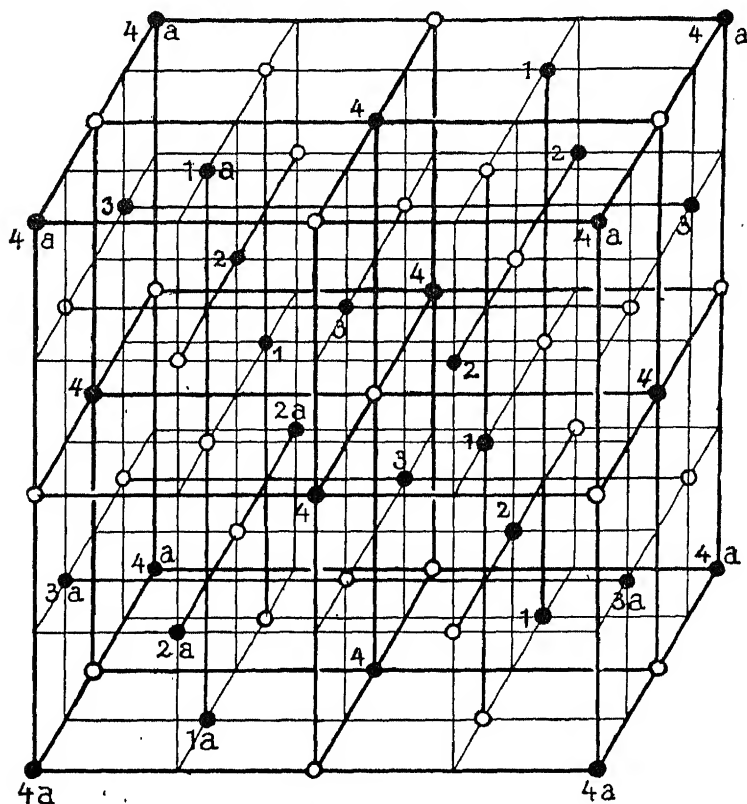
If we place in a regular $(8 \text{ Pg})_a$ three equal $(8 \text{ Pg})_a$ so that their points fall in the middle of the sides of the first lattice, this interpenetration of $4(8 \text{ Pg})_a$, is a $(14 \text{ Pg})_a$. In each of these $4(8 \text{ Pg})_a$, the points of the three others may be thought of as the center of the sides of the elementary cube of an $(8 \text{ Pg})_a$.

In this manner the $(14 \text{ Pg})_a$ is made up of the following partial lattices.

Number of Partial Lattices	Kind of Partial Lattice
4.....	$(8 \text{ Pg})_a$
8.....	$(14 \text{ Pg})_{2a}$
16.....	$(9 \text{ Pg})_{2a}$
32.....	$(8 \text{ Pg})_{2a}$
64.....	$(14 \text{ Pg})_{4a}$

The normal distribution for $p = m/8$. If we arrange a partial lattice $(8 \text{ Pg})_a$ and one $(14 \text{ Pg})_{2a}$ with A atoms, the normal distribution results for $p = 2/8$ and $1/8$. The normal distribution for $p = 4/8$

may not be reached by the same arrangement of two of the four $(8 \text{ Pg})_a$ but by that of four $(14 \text{ Pg})_{2a}$, and indeed these four lattices must be so related that on the lines of the cube sides the two kinds of atoms follow alternately, and further, the intersecting side diagonals of two cube planes must alternately possess only one kind of atoms.



$$p = \frac{4}{8}$$

FIG. 199

If the alternate diagonals with only one kind of atoms do not cross, a distribution of hexagonal symmetry results. The solid solution will then consist of alternate layers with only A or B atoms fitting in the lattice planes with equilateral triangles as meshes.

Fig. 199 gives the normal distribution for $p = 4/8$. Numbers on the black circles show the $(14 \text{ Pg})_{2a}$ to which they belong. The arranging of the partial lattices shown cannot be designated as regular

since the arranging of each group of four forms a tetrahedron with the smallest distance in the lattice that is not the same on the eight corners of the partial lattice. While two of the eight tetrahedra only are arranged with black atoms the others have two black and two white atoms. If we consider, however, the arranging of the greater part of the lattice we see that the center points of the tetrahedra are arranged only with atoms from a $(14 \text{ Pg})_{a\sqrt{2}}$ whose cube sides are parallel to the cube sides of the original $(14 \text{ Pg})_a$. The given distribution for $p = 4/8$ is normal if the lines of the cube sides and the body diagonals are alternately arranged with the two kinds of atoms. For two-side diagonals which are normal to each other and accordingly vertical to (011) the position of the three lines with the same fitting:

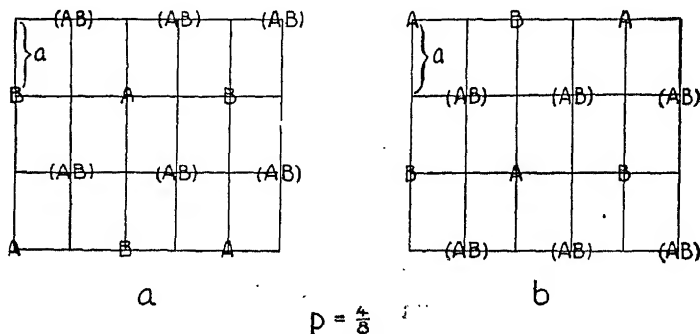


FIG. 200

$A, B, 2 (AB)$ is given in Fig. 200a and b; one position may be changed into the other by displacing the parameter a . The groups of similar packing are accordingly in the directions of the side diagonal.

The normal distribution for $p = 3/8$ may be arrived at in the following way. The A atoms in the lattice $p = 4/8$ lie on the intersecting side diagonals of the cube planes (Fig. 199). Each four of these

points are the vertices of a tetrahedron of the length of side $\frac{a}{2}\sqrt{2}$, each of these four points belongs to another $(14 \text{ Pg})_{2a}$. The points belonging to the same $(14 \text{ Pg})_{2a}$ are designated with figures 1-4. If a fourth of the A atoms all belonging to one of the four $(14 \text{ Pg})_{2a}$ are replaced, one of the four $(14 \text{ Pg})_{2a}$ will be different from the other three and the distribution cannot be normal. However, if a fourth of the four kinds of A atoms is replaced and each fourth of one kind belongs to a $(8 \text{ Pg})_{2a}$ the normal distribution will result. In Fig. 199 the replaced points are designated by a .

A complete survey of the distribution of the two kinds of atoms (black and white) is given by lattice models or their stereographic projections. In their place Figs. 201-204 show this distribution. They are partial cubic lattices portrayed on a diagonal plane directed toward

the observer. Table 43 gives the groups of lattice lines of the same arrangement in (14 Pg).

The symbol of a line that is fitted only with A-atoms is A, that of one with only B-atoms is B. The symbol of a line alternating with

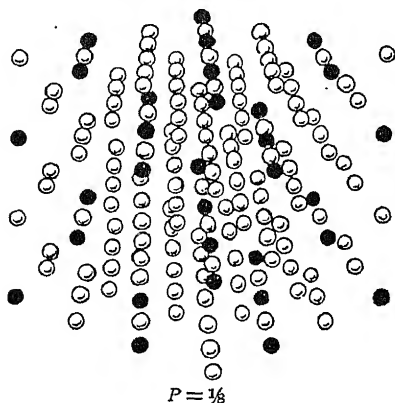


FIG. 201

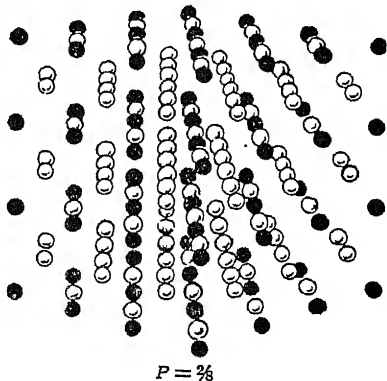


FIG. 202

A and B atoms is (A B), that of a line with an A-atom followed by three B-atoms is (A₃B) and that of a line with an A-atom followed by seven B-atoms is (A₇B), etc. The number of lines with these arrange-

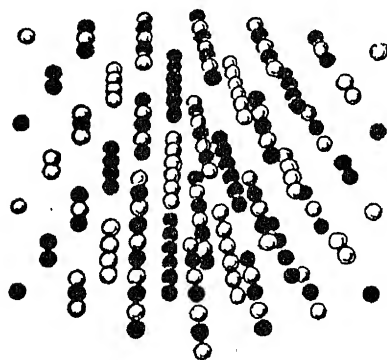


FIG. 203

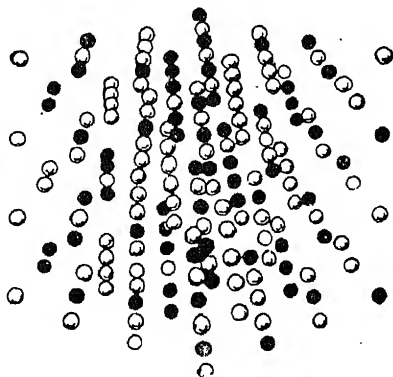


FIG. 204

ments which occur in a group is written before the symbol of the line. These simple designations are sufficient to fully specify the groups of the named directions for the normal distribution of the mol-fraction $p = m/2^n$.

TABLE 43

GROUPS OF THE LATTICE LINES OF THE SAME ARRANGEMENT IN THE 14-POINT LATTICE IN THE DIRECTION OF

p	The Cube Sides G_1	The Body Diagonals G_2	The Side Diagonals G_3
$\frac{1}{2}$	$15B, (AB)$	$15B, (AB)$	$7B, (A_3B)$
$\frac{2}{32}$	$7B, (AB)$	$15B, A$	$3B, (A_3B)$
$\frac{3}{32}$	$13B, 3(AB)$	$13B, 3(AB)$	$6B, (AB), (A_3B)$
$\frac{4}{32}$	$3B, (AB)$	$3B, (AB)$	$3B, (AB)$
$\frac{5}{32}$	$12B, A, 3(AB)$	$12B, A, 3(AB)$	$5B, 2(AB), (A_3B)$
$\frac{6}{32}$	$6B, A, (AB)$	$13B, 3A$	$2B, (AB), (A_3B)$
$\frac{7}{32}$	$12B, 3A, (AB)$	$12B, 3A, (AB)$	$4B, 3(AB), (A_3B)$
$\frac{8}{32}$	$3B, A$	$3B, A$	$B, (AB)$
$\frac{9}{32}$	$3B, 4(AB), (A_3B)$	$3B, 4(AB), (A_3B)$	$4B, 3(AB), (B_3A)$
$\frac{10}{32}$	$B, 2(AB), (A_3B)$	$B, 2(AB), (A_3B)$	$3B, 3(AB), (A_3B),$ (B_3A)
$\frac{11}{32}$	$2B, 5(AB), (A_3B)$	$2B, 5(AB), (A_3B)$	$4B, A, 2(AB), (B_3A)$
$\frac{12}{32}$	$B, 3(AB)$	$B, 3(AB)$	$B, (AB), (A_3B),$ (B_3A)
$\frac{13}{32}$	$B, 6(AB), (A_3B)$	$B, 6(AB), (A_3B)$	$B, 4(AB), 2(A_3B),$ (B_3A)
$\frac{14}{32}$	$3(AB), (A_3B)$	$3(AB), (A_3B)$	$2B, A, 3(AB),$ $(A_3B), (B_3A)$
$\frac{15}{32}$	$7(AB), (A_3B)$	$7(AB), (A_3B)$	$2B, A, 4(AB), (B_3A)$
$\frac{16}{32}$	(AB)	(AB)	$B, A, 2(AB)$

Survey of the distribution of two kinds of atoms in a space lattice. Four kinds of distribution of two kinds of atoms in a space lattice may be differentiated.

1. The normal distribution, that remains the same at temperatures where motion of the atoms takes place.

2. Abnormal distribution, whose symmetry is lower than that of the lattice. These are transformed at sufficiently high temperature into the normal.

3. Distributions which correspond to the symmetry of the lattice, in which however improbable aggregations of atoms of one kind occur. Since the occurrence of this distribution is more improbable the greater the aggregations of one kind of atoms it only occurs in small fields of the lattice for solid solutions at temperatures below that of the appreciable motion of the atoms.

4. The unoriented distribution of two kinds of atoms, that may occur due to the formation of solid solutions below the temperature of appreciable motion of the atoms if the two kinds of atoms are brought by any process into the arrangement of a lattice. Such processes are the precipitation of two kinds of metal-atoms by electrolysis and the evaporation of the solvent of two isomorphous bodies. Since the normal distribution can only occur under the action of the existing field of forces in a solid solution by the diffusion of the molecules or ions, if the diffusion is hindered the irregular rather than the normal distribution will be found.

To these four distributions in a space lattice two others may still be added.

5. Irregular distribution with oriented agglomerates consisting of one kind of atoms in the form of fibre or lamellae. It is possible that the solid solutions with abnormal double refraction which are formed in a temperature field with no diffusion possess such a structure.

6. In the abnormal distribution of the second kind, oriented agglomerates consisting of one kind of atom may occur in large fields of the lattice. Possibly meteoric Ni-Fe is a solid solution of this structure. (*Nachrichten d. Königl. Ges. d. Wiss. zu Göttingen* (1918), p. 258.)

Of these kinds of distribution only the normal is stable at temperatures where appreciable motion of the atoms takes place. The question whether the second kind of distribution is more stable than the fourth can only be decided by experiment.

8. Explanation of Reaction Limits.

Our problem is to explain on the basis of the normal distribution of two kinds of atoms in a space lattice the reaction limits found. For this a knowledge of the kind of lattice of the solid solution series of Au with Cu or Ag and of the solid solution series of Pd with Au and Ag is necessary.

According to the investigations of the Braggs and Vegard (W. L. Bragg, *Phil. Mag.* (6) 28, 355 (1915); L. Vegard, *Phil. Mag.* (6) 31, 83 (1916)) the atoms in copper and silver crystals are arranged in a cubic lattice whose corners and face centers have atoms, the 14-point lattice. The continuous series of solid solutions of copper with gold and of silver with gold would also be expected to have this lattice and according to Vegard (*Phil. Mag.* (6) 32, 65 (1916)) this is experimentally true. More recently Scherrer (*Phys. Zeitschrift* (19) 23 (1918)) has found the (14 Pg) for very finely divided gold. Since Pd as well as Au forms a continuous series of solid solutions with Ag its atoms are probably also arranged on a 14-point lattice.

The reaction process will be entirely different depending on whether the atoms of the reagent penetrate the solid solution or not. If the atoms of the reagent penetrate the solid solution two cases are possible. 1. The atoms of the reagent may penetrate the solid solution in any way whatever. Then a protective action will not be exerted by the metal that is not attacked, as in the precipitation of mercury out of mercurous salts by Cu-Au solid solutions where complete decomposition results. 2. The atoms of the reagent may penetrate the lattice of the solid solution only in a prescribed way, then a definite reaction-solubility limit must occur.

If the atoms or molecules of the reagent do not penetrate the solid solution its disintegration must proceed from the surface. In this connection it is to be remembered that with irregular distribution of two kinds of atoms in a lattice the reaction limit is not sharp but

extends over wide concentration intervals and that in these cases it must also be as quite high gold content as $4/8$ molecule. (See Fig. 198.)

(a) **Reaction limit of a reagent which penetrates the lattice.** In the solid solution series, Pd-Au, and Pd-Ag hydrogen is soluble in alloys containing 1.0-0.5 mole Pd.

By the penetration of hydrogen in the Pd-rich solid solutions the H_2 molecules are split into H-atoms that penetrate the Pd and its solid solutions. As a basis for this statement may be presented—

1. The equilibrium pressure in the system hydrogen-palladium is at small hydrogen concentrations proportional to the square of the hydrogen concentration in the palladium.

2. The solution velocity of hydrogen evolved on a Pd-cathode is very much greater than for H_2 gas.

If the H-atoms could enter and leave the solid solutions in any way whatever, the existence of a definite solubility limit of hydrogen in palladium solid solutions would not be understandable. If this motion, however, is limited by the condition that the H-atoms may only move inside the solid solutions in such a way that they jump from Pd atom to Pd atom and accordingly not to the foreign atoms we may explain the definite solubility limit in the following way.

If we take as a fibre a lattice line with only Pd-atoms and designate as the fibre ratio the number of fibres divided by the number of all lattice lines of one direction the following table gives a survey of the fibre ratios in the directions of the lines more thickly set with atoms for different mol-fractions p , of the Pd in the various solid solutions accordingly also a summary of the paths which the H-atoms have at their disposal.

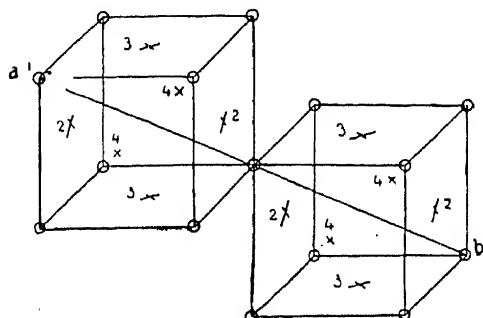
Ratios of elementary fibres in 14-point lattice with normal distribution of two kinds of atoms.

	$p = 7/8$	$5/8$	$3/8$	$1/8$	0	$1/8$	$3/8$	$5/8$	$7/8$
1 Side diagonals normal (011).....	0	0	$1/8$	$1/4$	$1/4$	$1/2$	$3/4$	$5/8$	$7/8$
2 Cube sides vertical (001).....	0	$1/4$	0	0	$1/4$	$3/4$	$5/8$	$7/8$	$7/8$
3 Body diagonals three corners face centers normal (211).....	0	0	$1/8$	$1/4$	$1/4$	$1/2$	$3/4$	$5/8$	$7/8$
4 Body diagonals through the cube corners normal (111).....	0	$1/4$	0	0	$1/4$	$3/4$	$5/8$	$7/8$	$7/8$

In directions 1 and 3 the fibres first disappear with a Pd-content of $2/8$ molecule. Since the limit of solubility lies at $4/8$ molecule these fibres must not be the path of the H-atoms.

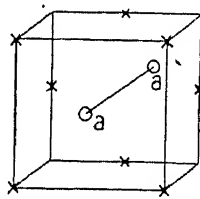
In the directions 2 and 4 the fibres occur again at $2/8$ and $1/8$ molecule Pd. Fibers accordingly occur here in a field in which the H-atoms no longer penetrate the solid solutions, afterwards they disappear between $4/8$ and $2/8$ molecules. The surroundings of the fibres between $2/8$ and $1/8$ molecule Pd prevents the H-atoms in their movement along these fibres.

The surroundings of fibres of the body diagonal and the cube side in the normal distribution for $p = 2/8$ molecule Pd are shown in Figs. 205 and 206. The circles designate the Pd atoms, the crosses Au or Ag atoms. If a H-atom would move on the line ab , a fibre of the body diagonal, Fig. 205, to pass from the first to the second atom it must twice pass the narrow gap formed by three crosses 2, 3, 4. The crosses are arranged at the vertices of the equilateral triangles in the octahedral planes to which the fibre is vertical, and the side of the equilateral triangle that the crosses 2, 3 and 4 form is equal to the smallest distance of two lattice points $a/\sqrt{2}$.



$$p = \frac{2}{8}$$

FIG. 205



$$p = \frac{2}{8}$$

FIG. 206

If a H-atom would move along the parallel to the cube side arranged only with Pd atoms a , Fig. 206, it must pass through a square whose corners have crosses, and indeed to pass from the first to the second Pd-atom it must pass through two superposed squares rotated 90° with respect to one another and whose side length is equal to the parameter a .

From the fact that the solid solutions with $2/8$ to $1/8$ molecule Pd at temperatures where appreciable motion on the Pd-atoms does not take place do not absorb hydrogen, and the circumstance that the fibre surroundings described for $4/8$ mole Pd are no longer present we conclude that the added element hinders the penetration of the H-atoms.

The parameter of the Pd-lattice cannot be very different from that of the copper lattice 3.61×10^{-8} cm. According to P. Debye the diameter of the electron ring in the H_2 molecule is 1.05×10^{-8} cm. The H-atoms could accordingly pass the described gaps if forces did not occur which hindered them.

If the Pd-content exceeds $4/8$ mole there result in the direction of cube sides and body diagonals, bundles of fibres in which the H-atoms can penetrate the solid solutions. With very small excess of the Pd-content over $4/8$ mole these fibre bundles are long but occur seldom, with increasing Pd-content they are shorter but more

frequent. There is also a possibility of the H-atoms migrating from one fibre bundle to another.

(b) Reaction limits of reagents that do not penetrate the solid solutions. With solid solutions of Au with Cu or Ag the reaction limits are frequently at $4/8$ and $2/8$ mole Au and less frequently at $1/8$ mole Au, which limit is observed for the Ag-precipitation from Ag solutions by Cu-Au alloys also probably for the precipitation of Os out of a solution of OsCl_4 .

The question why the reaction limits are so different for different agents is answered by reference to the different number of active atoms of the solid solution which a molecule of the reagent requires to enter into reaction.

If the reagent require four Cu atoms it can find four neighboring atoms on a cube plane, if the Au content of the Cu-Au solid solution falls below $1/8$ mole. In the normal distribution for $1/8$ mole the cube plane is arranged in the way shown in Fig. 207 and the

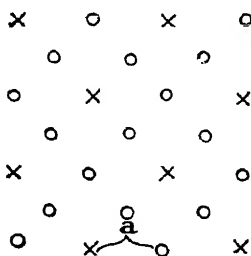


FIG. 207

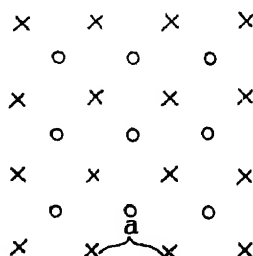


FIG. 208

following cube lattice planes are only arranged with Cu-atoms. We see that four Cu-atoms (circles) whose distance from each other is $a/\sqrt{2}$ are not present in the lattice plane, Fig. 207. First if one of the Au-atoms (crosses) is replaced by a Cu-atom the condition for reaction is fulfilled. As a result of the reaction a breach forms in the lattice plane, Fig. 207, of surface area $(2a)^2$ through which the reagent enters to a second lattice plane arranged only with Cu-atoms. By the replacement of an Au-atom 8 Cu-atoms are accordingly subjected to the reaction. On the octahedral or rhombic dodecahedral planes this ratio is entirely similar since according to Table 43 the groups of lines of the same arrangement in the directions vertical to them are the same as in the direction of the cube sides.

If a reagent requires two Cu-atoms it can find them on a cube plane with the distance $a/\sqrt{2}$ only when the Au content falls below $2/8$ mole. In the normal distribution for $2/8$ mole Au one cube plane is arranged as shown in Fig. 208 and the following lattice planes contain only Cu-atoms. We see that two Cu-atoms with the distance $a/\sqrt{2}$ are not present in the lattice plane, Fig. 208. If one of its Au-atoms

(crosses) is replaced the reagent may react with two atoms and remove them from the lattice, whereby the possibility of reaction with two copper atoms of the following plane is made possible. By replacing one Au-atom, four Cu-atoms are rendered susceptible to reaction. On the rhombic dodecahedral planes the distribution is entirely similar to that on the cube planes. On the octahedral planes a plane arranged entirely with Cu-atoms follows an alternately arranged plane and since the distance of all copper atoms from each other is $a/\sqrt{2}$ they will be susceptible to reaction. If the Au-atoms with the distance $2a/\sqrt{2}$ retain their place in the lattice they will protect the Cu-atoms in the following lattice plane.

A reagent that can react with only one Cu-atom finds single copper atoms on the surface of the solid solution richest in gold. If after removing the Cu-atoms the Au atoms retain their place in the lattice, the molecules of the reagent are prevented by them from acting on the deeper lying copper atoms. Since the removal of a few copper atoms out of the surface cannot be detected, the solid solutions in which the gold atoms retain their place in surface appear resistant. If we conceive of an Au-atom in a cube plane of the normal distribution for $p = 4/8$ as replaced with a copper atom, a way is opened for the reagent to get to the copper atoms at the corners of a tetrahedron with the side $a\sqrt{2}$ and by the collapse of the Au-atoms under which the copper atoms have been removed the breach is widened.

The reaction limits for reagents that need one, two or four copper atoms for their reaction can be understood on the basis of the normal distribution in a (14 Pg)_a. Further the number of Cu- or Au-atoms which the reagent can react with is as a rule determined by the valence of the reagent. The reagents which require one Cu- or Ag-atom as nitric acid, AuCl or AuCl₃ solution and a dilute solution of FeCl₃ may be considered as monovalent reagents, while sulfur and selenium containing solutions as well as weak oxidizing agents in which the S, Se or O require two Cu- or Ag-atoms for reaction are known as bivalent reagents. The action of silver salts which would be expected to have the reaction limits of monovalent reagents is surprising since they act like the quadrivalent reagents (OsCl₄).

Out of the solid solutions of gold with Cu or Ag the Cu or Ag is completely removed by nitric acid up to $3/8$ mole. From $3/8$ mole Au up, however there remains an amount of Cu or Ag which increases with the Au-content. From $4/8$ mole Au the amount remaining is the original amount present. The explanation for the fact that from $3/8$ mole down all the copper or silver may be removed is to be sought in the circumstance that a series of three consecutive Au-atoms on the side diagonal of the cube plane do not retain their place but separate from the lattice; thereby the lattice planes parallel to the cube planes are completely disintegrated. In the distribution for $p = 4/8$ the alternate side diagonals of the cube plane are arranged only with Au- or only with Cu-atoms. If the Au content falls to $p = 3/8$, every

fourth atom in a series of gold atoms is replaced with a copper atom. If here all the Cu-atoms of the cube plane are removed by nitric acid, the three consecutive Au-atoms will no longer retain their places and the action of the reagent on the following lattice plane with the same arrangement begins, etc. With an Au-content between $3/8$ and $4/8$ mole there remain still groups of Au-atoms with more than three Au-atoms which protect part of the lattice from the reaction. The relations on the surface of the rhombic dodecahedron and the octahedron are very similar.

There remains still to mention the reaction limits $6/8$ and $7/8$. The solid solution with $7/8$ mole of the more noble component is, of the solid solution series with normal distribution, the poorest in the nobler component, in which the planes more dense with atoms (cube, octahedron and rhombic dodecahedron) are alternately free from the atoms of the less noble component. Therefore the reagent cannot reach the less noble atoms, it will only be able to disintegrate the planes with active atoms and its action will then be stopped. An example for this case is the action of a silver solution on the solid solutions of Mg and Ag.

In solid solutions with $6/8$ mole of the inactive component, alternate cube planes are arranged only with the inactive atoms, the same holds for the lattice planes parallel to the planes of the rhombic dodecahedron. On the octahedral planes, however, the arrangement of the lines parallel to the sides of the octahedron is as follows: a line arranged only with inactive atoms followed by an alternately arranged one. A reagent that is active up to $6/8$ mole of the inactive component will accordingly begin a deep going action on the octahedral planes and its action will by the removal of the active atoms, cause gaps so that the deeper lying atoms may be acted upon, while a reagent that reacts up to the limit $7/8$ mole lacks this possibility. If the content of the inactive component falls below $6/8$ mole active atoms occur on the lattice planes of the cube and dodecahedral planes which were arranged only with inactive atoms. This makes possible the deeper reaction of the reagent. It is therefore necessary to introduce a special conception to explain the cause of the reaction limits of $7/8$ and $6/8$ mole of the inactive component.

If we wish to classify the reagents according to their reaction limits they may be called quadrivalent, bivalent and univalent according to whether they need four, two or one atom of a univalent metal for their reaction. This degree of reaction of a reagent is apparently not independent of the nature of the inactive metal.

We cannot therefore predict with certainty up to what limit a reagent will react, if the reaction limit of an entirely analogous reaction on the same solid solution series is not known. The reaction limit appears to be displaced to higher contents of the inactive components the further the two components are separated in the electromotive series.

The explanation of the reaction limits is a stereometric-atomistic one, being derived from the normal distribution of two kinds of atoms in a lattice. The conserving force of the lattice is arrived at, through the assumption, that after removal of the active atoms from the surface, the inactive remain in the lattice and thereby protect the deep lying active atoms. If this condition is not fulfilled, reaction takes place as e.g. in the action of reagents containing sulfur on Ag-Au solid solutions. The failure to reach a normal reaction limit as by the action of reagents containing oxygen on the Cu-Au solid solutions may be traced to the fact that in its neighborhood a residue of the copper atoms of the surface combine with oxygen atoms, which nevertheless remain in the lattice.

9. Space Lattice Isomerism.

If two metals precipitate simultaneously in a temperature region in which appreciable movement of the atoms does not take place, the normal distribution cannot take place but an apparently random dis-

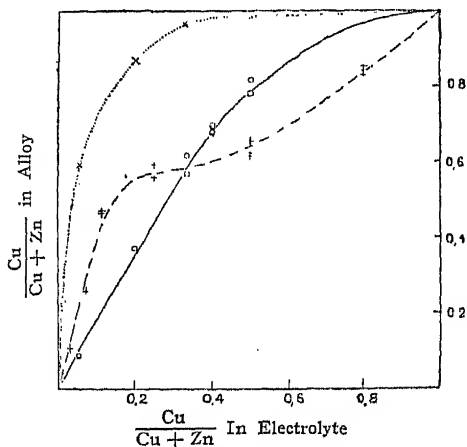


FIG. 209

tribution results. It is therefore apparent that the normal stable arrangement is not at once prepared by arranging the atoms in a space lattice but owes its existence to the field of force of the solid solution.

Observations concerning the precipitation of two metals out of solution forming crystalline or cryptocrystalline products have been made, however the properties of these products cannot be compared with those which result by melting the two metals together since up to now the observations have been made in cases where the alloy series which result from the melt are known only partially or not at all. Crystalline binary metal mixtures may be obtained from the solution of the

two metals by electrolysis or by the precipitation with less noble metal.

(a) Cathodic precipitation out of a binary electrolyte. If the two metals in the electrolyte are far apart in the electromotive series, at small current densities only the nobler metal will be precipitated, at higher current densities both metals precipitate and at very high current densities both precipitate in the ratio in which they are present in the electrolyte. If a mixed solution of CuSO_4 and ZnSO_4 (total amount 1 mole per liter) is electrolyzed with a current density of 0.1 amp. per sq. cm. of cathode, the relation of the composition of the

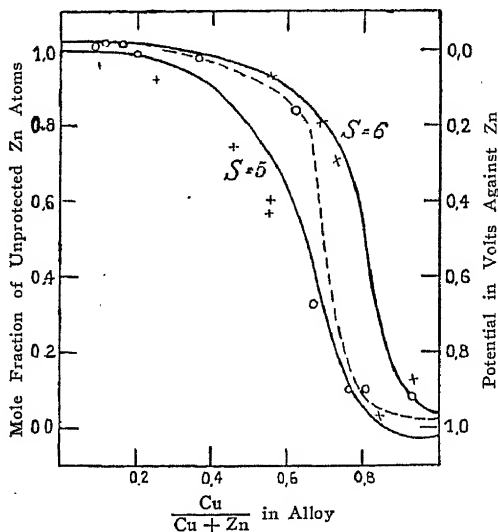


FIG. 210

material precipitated at the cathode to the composition of the electrolyte will be as shown in Fig. 209. The dotted curve represents this relation for a small current density. A solution of 0.2 mole ($\text{ZnCu}_2 + \text{CuCy}$) and 0.4 mole KC_y per liter is represented by the broken curve.

If we determine with an electrometer the e.m.f. of this crystalline deposit against Zn in ZnSO_4 we obtain for the deposition out of a solution of the mixed sulfates the circles as in Fig. 210 and for deposition out of solution of the cyanides the crosses in this figure. If the previously given curves $S = 5$ and $S = 6$, which give the fraction of unprotected zinc atoms for various ratios of Zn and Cu for a random distribution of both kinds of atoms in the lattice, are transferred to this diagram we see that the potential of the deposits containing Zn and Cu changes with their composition as the mole fractions of the Zn atoms not protected by copper. The difference in the potential of the deposits from sulfate and cyanide solutions may be

traced to their difference in structure. While the deposits prepared from sulfate solutions are crystalline powders with a large surface, out of a cyanide solution a coherent layer forms with very much smaller surface, and out of which the zinc atoms disappear more rapidly due to the oxygen present in the solution, than out of deposits with greater surfaces for whose oxidation the oxygen present is not sufficient. As a result of this the precipitates out of cyanide solutions appear more noble than those out of sulfate solutions (F. Sauerwald, *Z. anorg. Chem.* **111**, 267 (1920)).

If we compare the potential-concentration curve *a*, of the electrolytic deposits with the corresponding broken line for alloys obtained by melting together the metals, Fig. 211, we see that they are markedly

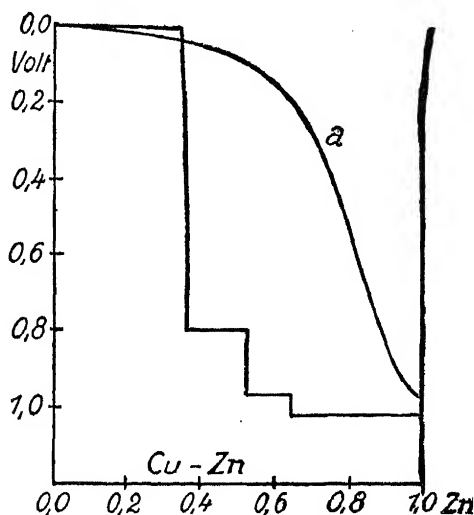


FIG. 211

different. Correspondingly, the chemical properties of these alloys are entirely different, especially in their behavior toward solutions of other metals. The basis of this difference is the different arrangement of the Cu and Zn atoms in the lattice. In the electrolytic preparation of alloys the distribution of the two kinds of atoms is a random one and in those obtained by melting it is normal.

The potential-concentration curve of the two metals precipitated electrolytically is specified by a whole number *S-1* the number of noble atoms which protect the less noble (compare the formula, p. 315). This number determines the course of the potential-concentration curve (Fig. 210). For the electrolytic deposits of the following metal pairs the following numbers give the atoms of noble metal necessary to protect one of less noble.

Cu-Cd	4
Cu-Pb	4
Cu-Zn	5
Ag-Cu	7
Cu-Fe	22

(b) The precipitation of a more noble metal out of a dilute solution by a less noble. The precipitation from very dilute solutions of more noble metals by less noble ones have been investigated by Mylius and Fromm (*Ber. d. Chem. Gesell.*, Berlin, 27, 630 (1897)) who detected in them a considerable amount of the precipitating metal. In several cases the composition of the precipitates approaches that of definite compounds which form out of the melt, but the precipitates differ from these in their properties. Apparently these precipitates are identical with those formed by electrolysis of mixed electrolytes. The composition of both depends on that of the mixed electrolyte and the current density at the place of precipitation. By the precipitation of one metal by another there is formed a mixed electrolyte and a short circuited galvanic cell. Since the composition of the mixed electrolyte and the current density of this cell can only vary within narrow limits, the composition of the resulting precipitate is only slightly variable. That these precipitates differ very much from the alloys of the same composition obtained from a melt can be seen from the following comparison.

Cu_3Sn . The beautiful blue green crystals of Cu_3Sn with 38 per cent. Sn as formed from a melt, precipitates only metals which copper precipitates; the precipitate from a dilute solution of CuCl_2 by Sn contains 36-39 per cent. Sn. In a solution of HCl or H_2SO_4 it becomes quickly covered with CuCl or CuSO_4 and shows a very much smaller potential against Sn than the crystals formed from a melt.

Au-Ag . From a solution of AuCl_3 (2.5 g. of Au in 500 c.c.) by precipitation with silver foil a deposit containing 12.5 per cent. Ag is obtained. The AgCl incidentally formed may be extracted from the precipitate by NH_4OH . Practically the entire silver content of this precipitate may be removed quickly by nitric acid; it also precipitates Au and Pd out of their solutions while the Au-Ag alloy containing 12.5 per cent. Ag resulting from a melt is not attacked by nitric acid nor will it precipitate Au or Pd. If the precipitate is heated for 10 minutes at 700°C . it will be transformed to the normal distribution and the powder will not be appreciably attacked by nitric acid.

It is accordingly possible to prepare crystalline alloys electrolytically which are entirely different from those formed by melting together the metals. The space lattice of these pairs of alloy series need not be the same. Still the difference in the kind of the two lattices will not explain their different properties since the difference of potential of the same metal in two different lattices is very small. According to E. Cohen (*Z. physik. Chem.* 30, 628 (1899)) the potential of ordinary tin against gray tin at 15° supercooling amounts to only

0.00077 volt. Therefore there remains as a basis for the very different behavior of the two alloy series only a difference in the distribution of the two kinds of atoms in the lattice. From the conditions of formation of the two series it follows that the electrolytically prepared alloys will have a random distribution in the lattice and those formed from the melt a normal. If the alloys with a random distribution of the atoms are brought into a temperature region where there is an appreciable motion of the atoms, they go over to the normal distribution and the alloys are identical with those formed from the melt.

10. The Potential of Alloys.

(a) **Equilibrium theory.** From the existence of chemical resistance limits in solid solution series it follows that resistance limits also exist for the potential of solid solution series. The thermodynamic theory of the dependence of the potential of the alloy on its composition is in apparent contradiction to the existence of resistance limits for the potential. This theory can naturally only be applied if the metallic phase is in equilibrium with the electrolyte or if in the metallic phase the motion of both kinds of atoms is sufficient for the preparation of a definite concentration. These conditions are not met with at the temperatures where chemical resistance limits occur and there still remains the question of whether the rules for solid solution and alloy series hold in this temperature range.

We will begin with a short discussion of the thermodynamic theory, and follow with examples of the electrometric and galvanic relations of the Ag-Au solid solutions and compare the potential lines with the micro-structure of the alloy series and finally refer to the atomistic theory of the potential lines. The conditions for the equilibrium of a binary heterogeneous metallic mixture with an electrolyte that contains the two metals as ions have been given by W. Nernst in the form of equations (*Z. physik. Chem.* 22, 539 (1897)) and Reinders has interpreted these equations graphically (*Z. physik. Chem.* 42, 225 (1903)).

The potential of a metal in a solution in which its solution tension is P and the osmotic pressure of its ions is p and n is the valence of the ions, R the gas constant, F the charge on a gram equivalent of the ion and T the absolute temperature is represented by the equation,

$$\pi = \frac{RT}{nF} \ln \frac{P}{p}$$

If equilibrium occurs at an electrode containing two metals the osmotic work of transporting one kind of ion in the solution and the other in the metallic mixture must neutralize each other, accordingly

$$\pi = \frac{RT}{n_1 F} \ln \frac{P_1}{p_1} = \frac{RT}{n_2 F} \ln \frac{P}{p_2} \quad (1)$$

Here P_1 and P_2 designate the partial solution tensions of the two metals in the metallic mixture, p_1 and p_2 the partial osmotic pressures of the two kinds of ions in the electrolyte.

If both kinds of ions are univalent then $n_1 = n_2 = 1$, then

$$\pi = \frac{RT}{F} \ln \frac{P_2}{P_1} = \frac{RT}{F} \ln \frac{p_2}{p_1}. \quad (2)$$

The partial solution tensions of the two metals in their mixture behave then as the osmotic pressures of the two ions.

The potential of the binary metallic mixture depends accordingly on the ratio of the partial solution tensions and on the ratio of the ion concentrations in the electrolyte and will, for a definite concentration of one of the two kinds of ions be shown by two curves. One of these gives the potential in relation to the mole fraction of the metallic mixtures $\pi = f(x_m)$, the other in relation to the mole fraction of the electrolytes, $\pi = \varphi(x_e)$. If we are dealing with the equilibrium of an alloy with two kinds of ions that are dissolved in a third substance there is a pair of each kind of curves for the arbitrarily variable concentration of one kind of ion. If we are dealing with mixtures of two electrolytes, e.g. two molten salts, this variability disappears since the concentration of both kinds of ions is then determined.

To get an approximation of the form of these curves we must assume either a relationship of P_1 and P_2 to x_m or else of p_1 and p_2 to x_e . If we assume that for the relation between the partial solution tensions and x_m , the law of vapor pressure lowering holds, and that the osmotic pressures p_1 and p_2 are proportional to x_e and $1 - x_e$ we may write: $P_1 = (P_1)(1 - x_m)$ and $P_2 = (P_2)x_m$ where (P_1) and (P_2) are the solution tensions of the two metals, then

$$\frac{P_2}{P_1} = \frac{(P_2)x_m}{(P_1)(1 - x_m)} = \frac{P_2}{P_1} \cdot \frac{x_e}{1 - x_e}. \quad (3)$$

If P_2 , x_m , p_2 and x_e belong to the less noble metal with the larger solution tension then as a rule P_2 will be very large compared to P_1 and therefore the tension

$$\pi = RT \ln \frac{(P_2)}{(P_1)} \cdot \frac{x_m}{1 - x_m}$$

will increase at first rapidly and then more slowly with x_m .

For the curves $\pi = \varphi(x_e)$ it follows from (3) that the ratio,

$$\frac{x_e}{1 - x_e} = \frac{P_2}{P_1}$$

and similarly the potential $\pi = \frac{RT}{F} \ln \frac{P_2}{P_1}$ increases at first slowly and then more rapidly with x_e . Fig. 212 shows the two curves $\pi = f(x_m)$ and $\pi = \varphi(x_e)$ for a continuous series of solid solutions. The $\varphi(x_e)$ curve is dotted as in the following diagrams,

If a gap occurs in the series of solid solutions the potential of the two saturated solid solutions will be equal and all conglomerates consisting of them will have the same potential. The potential of the two saturated solid solutions may however be larger or smaller than

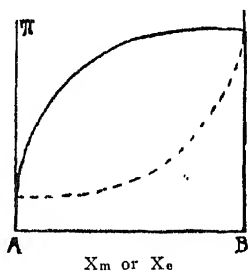


FIG. 212

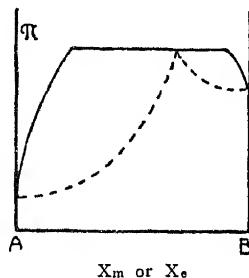


FIG. 213

that of the less noble metal. In the first case, diagram Fig. 213 holds, in the second Fig. 214.

If the two metals form a compound that forms practically no solid solutions with its constituents there is a discontinuity in the $f(x_m)$ line at the composition of the compound and in the $\varphi(x_e)$ line there is a minimum when $x_m = x_e$ (Fig. 215).

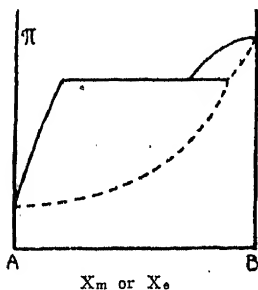


FIG. 214

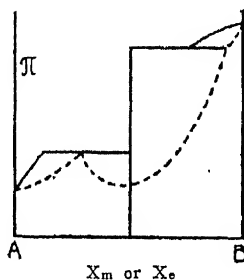


FIG. 215

From the diagrams we get for each potential π the composition of the alloy x_m and the electrolyte x_e that are in equilibrium. Precipitation or solution of the alloy proceeds according to whether the potential is greater or less than the equilibrium potential. If a parallel to the x axis is passed through the given value of the π the intersection of the abscissae with the $f(x_m)$ and $\varphi(x_e)$ lines give the concentrations sought.

The coördinates of the $f(x_m)$ lines are easy to determine if the equilibrium potential is known; the determination of the $\varphi(x_e)$ lines is more difficult.

Of the alloy series to which the thermodynamic theory may be applied apparently only two have been investigated. That of the Cd-Hg series by Bijl (Fig. 216) (*Z. physik. Chem.* 41, 641 (1902)), for which Bijl has also worked out the equilibrium diagram and that of the Ag-Hg amalgams by Reinders (*Z. physik. Chem.* 54, 609 (1907)) for which the equilibrium diagram is unfortunately lacking.

In agreement with the theory it has been found—

1. That alloys consisting of two kinds of crystals have a potential independent of their composition.

2. The potential lines $f(x_m)$ of solid solution series are continuous curves, which as the theory requires rise rapidly for the nobler alloys and slowly for the less noble.

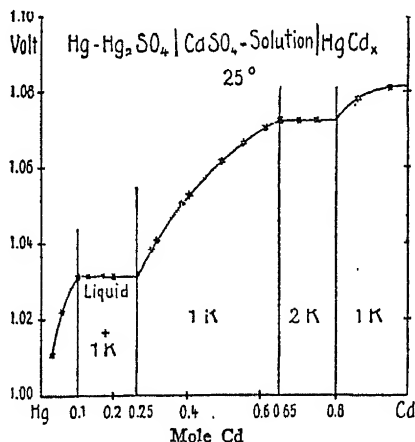


FIG. 216

3. If a discontinuity occurs in the potential it corresponds to the occurrence of a new kind of crystal.

This theory holds however only for reversible equilibria and these only exist if the two kinds of atoms in the metallic crystal can interchange positions.

In the temperature range of 0-100° this theory is only applicable to amalgams and other especially low melting alloys. For the greater part of the metallic substances its application is still in question since from the occurrence of resistance limits in solid solution series of higher melting metals it follows that in these solid solutions an appreciable motion of the atoms does not take place.

(b) The potential-concentration lines with slight diffusion in the solid solutions. 1. Homogeneous Mixtures: Galvanic cells which consist of a base metal, the solution of a salt of this metal and the members of an alloy series show an entirely different behavior depending on whether diffusion takes place in the electrode or not. If

diffusion takes place the potential increases rapidly by the addition of small amounts of the less noble metal to the nobler and reaches a value practically that of the less noble. This behavior is found in amalgams in which diffusion takes place at ordinary temperatures. Very small

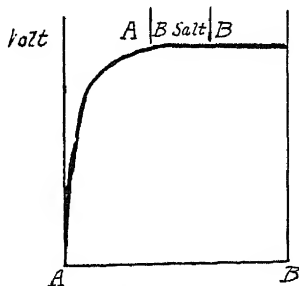


FIG. 217

amounts of less noble metals as Zn, Cd, Tl, Pb or Sn give to mercury the potential of these metals. We would expect the same for all alloy series at high temperature if they form a continuous series of liquid or solid solutions. In this case the relation of the composition to the

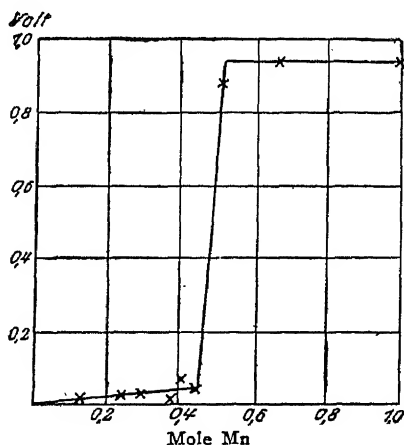


FIG. 218

potential is given in Fig. 217. The component A is the noble metal, B the base. The first addition B to A increases the potential greatly and further additions less.

The conditions are entirely different at temperatures where the diffusion is no longer appreciable in a continuous series of solid solutions. Then the added base metal, if it is less noble than hydrogen,

disappears as a result of interaction with moist air and the upper atomic layer contains only atoms of the noble metal. Correspondingly the alloy series shows a potential that up to a certain concentration does not differ from the noble component. An example of this case is the Cu-Mn alloys whose potential line in relation to the Mn content is given in Fig. 218. From 0-0.5 mole Mn this continuous series of solid solutions shows the potential of Cu at 0.5 mole, it increases to that of Mn and remains unaltered up to 10 mole Mn. The chemical relations of the Cu-Mn series are also in agreement with this. The alloys with more than 0.5 mole Mn precipitate metals that are more noble than Mn and less noble than Cu, while alloys with less than 0.5 mole Mn precipitate only those more noble than Cu.

The continuous series of solid solution of Cu-Au behave somewhat

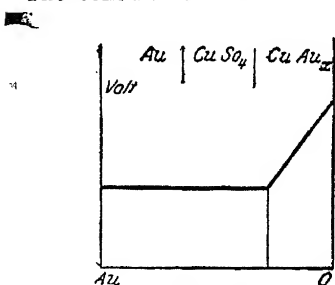


FIG. 219

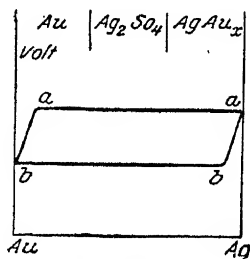


FIG. 220

differently, Fig. 219. For the alloys from 1.0-0.25 mole Au the potential increases practically linearly with increasing copper content which is apparently due to the fact that the surface of these alloys is covered with Au dust. The limit of 0.25 mole Au up to which the potential of gold is observed is practically coincident with the chemical reactivity limit for the action of weak oxidizing reagents and sulfur containing reagents on Cu-Au alloys.

In the Ag-Au alloys which are also a continuous series of solid solutions the less noble component is not attacked by aerated water, as is Cu, hence the Ag atoms are not removed from the surface of these alloys and the electrometer shows that these alloys have the potential of silver up to very high gold content, Fig. 220, line *a a*. If the Ag-atoms are removed from the surface by immersing in nitric acid the electrometer shows the Au-potential, line *b b*, even in silver rich alloys. If the alloys are heated the Ag atoms diffuse to the surface and the Ag-potential is again observed. The surface of these alloys can accordingly be made to give either the Au or Ag potential at will. The electrometer only tells us whether atoms of the less noble metal occur in the surface layer. A change in the color of metal bars on change of potential is not to be noted.

2. Solid Solutions with Gaps: In temperature fields where no diffusion of the two kinds of atoms takes place, the potential of a

series of solid solutions is independent of their composition. This also holds true in general for alloy series which consist of two kinds of crystals whether diffusion takes place or not. Since in practically all alloy series with the exception of amalgams the diffusion at ordinary temperature is not appreciable, the constancy of the potential with change of composition is no criterion for establishing the micro-structure of the alloy. On the other hand at high temperature where diffusion is appreciable, the potential of a solid solution series varies along a curve, while with two kinds of crystals it does not change with the composition.

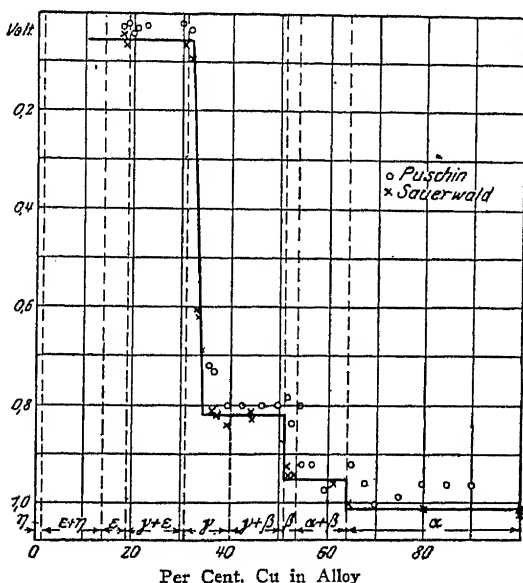


FIG. 221

As an example of this and of the great change of potential with the temperature, we will consider these lines for the Zn-Cu alloys. Fig. 221 gives the potential line at 18°, Fig. 222, at 380°. At 18° the potential within the α solid solution series against Zn in ZnSO₄ solution is independent of the composition. With the occurrence of the β -solid solution it decreases 0.01 volt. This difference is due to the difference of the space lattice of the α and β solid solutions. The influence of the occurrence of γ -solid solutions is unusually great, the potential decreasing more than 0.1 volt. A large potential change takes place in the γ -solid solution series. This has been erroneously ascribed to a compound. After the potential rapidly falls to almost that of zinc it changes no further in the ϵ -series and falls only slightly

with occurrence of η -crystals, thus reaching the potential of zinc. The chemical behavior of the Cu-Zn alloys corresponds to the course of the potential lines. From 100-38.3 per cent. copper the alloys neither precipitate Cd, Tl and Pb nor evolve gas with acids, while from 0-35 per cent. these reactions occur.

The sudden decrease of potential does not occur here at a rational mole fraction of Cu. $1/3$ mole Cu corresponds to 32.7 per cent. and $3/8$ mole to 36.35 per cent. while the decrease comes between 33.5 and 34 per cent. Cu (Sauerwald, *Z. anorg. Chem.* **111**, 257 (1920).)

The potential curve at 380° is entirely different since at this tem-

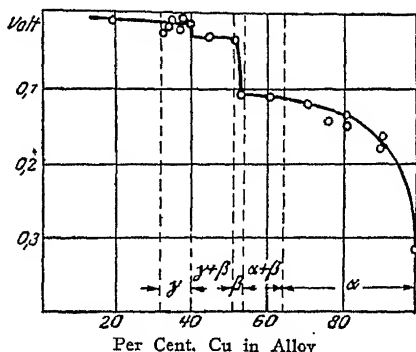


FIG. 222

perature the motion of the Cu and Zn atoms in the space lattice is quite free. Here the potential measured in molten ZnCl_2 against Zn decreases with increasing zinc content at first rapidly, then slowly, Fig. 222. In the alloy series which consist of α and β crystals the potential is independent of the composition, it falls considerably in the β -series and is constant in the series $\gamma + \beta$. In the γ -series there is no decrease of potential. Quite similar relations are to be found for Cd-amalgams.

The measurements of Puschin (*Z. anorg. Chem.* **56**, 1 (1908)) on alloys of Au with Sn and Zn as well as Ag with Sn and Zn, gave results that could not be connected with the micro-structure on the basis of the equilibrium theory. A chemical investigation of continuous series of solid solutions gives explanation of this. The constancy of the potential in the Au-Ag rich alloys is a result of the lack of diffusion whereby a protective action of the noble metal on the less noble is possible. The practically discontinuous change of potential in the solid solutions of Zn-Au from 0.45-0.64 mole Au, at 0.5 mole Au, Fig. 223, and the similar change for the series Zn-Ag from 0.11-0.29 mole Ag, at 0.25 mole Ag is a result of protective action.

At higher temperatures where there is a motion of the atoms and the conditions of the thermodynamic theory are fulfilled, the potential line must have a different form. Fig. 224 gives this for an imaginary

case. B is the nobler component and the two components form a solid solution series with a gap $2K$. At low temperatures the potential

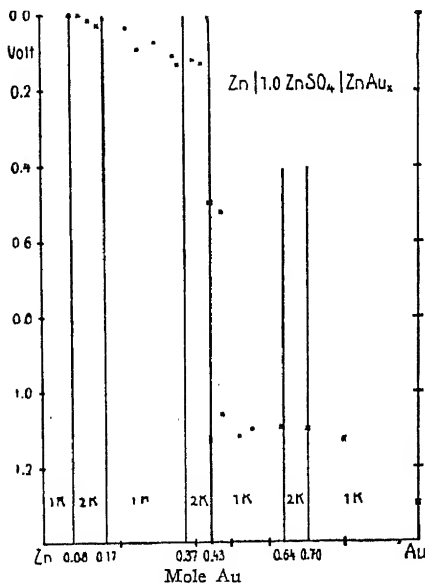


FIG. 223

curve 1 holds, at high temperatures the potential curve 2. In agreement with the thermodynamic theory, the addition of the less noble component lowers the potential at first rapidly and then slowly, while in

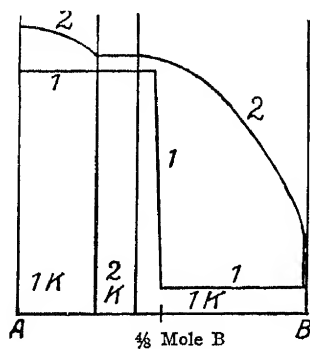


FIG. 224

the potential line 1, the potential of the two series of solid solutions is independent of their composition and changes at the reaction limit $4/8$ mole B .

With the absence of appreciable motion of the two kinds of atoms in the space lattice, the potential is independent of the concentration up to the beginning of the rapid fall of the potential, the galvanic reaction limit. If a gap occurs in this part of the solid solution series, the two end members of the gap have the same potential if they have the same lattice. If the lattices of the two series of solid solutions are different and the galvanic resistance limit does not fall in the gap, by decreasing the amount of the nobler component, a small discontinuous decrease in potential will take place at the limit of the miscibility gap. This change may however be so small that it is difficult to establish. On the other hand if the resistance limit falls in the miscibility gap there will be a jump from the potential of one component to that of the other no matter whether the two series of solid solutions have the same or different lattices.

(c) Determination of slight solubility of a base metal in the crystals of a noble one. Since the solid solutions, which are rich in the noble component, show the potential of this component against the less noble, the potential must fall to zero by the decrease of the content of the nobler component below that of the saturated solid solution, if here the crystals of the less noble component or a non-resistant kind of crystals occur. This fall of potential corresponds to a change in the microstructure of the alloy. The alloys which show the potential of the nobler component consist only of solid solutions, as soon as the potential falls to zero another kind of crystal forms. From the observations of Herschkowitz (*Z. physik. Chem.* 27, 123 (1898)) the following solubilities in the nobler component may be deduced. Closer values have been established by P. Fuchs (*Z. anorg. Chem.* 109, 80 (1920)) and the conclusion reached, that at the drop in potential a change in the microstructure takes place, viz., the formation of the eutectic.

Cd-Sn	0.015-0.025 mole Cd
Cd-Pb	0.085-0.095 " "
Cd-Bi	0.001-0.003 " "
Zn-Bi	0.075-0.085 " Zn
Zn-Sn	0.02 -0.03 " "

(d) The potential concentration lines for the occurrence of singular crystal species (compounds). In solid solution series with normal distribution of both kinds of atoms, one part of the series behaves as one component and the other part as the other component. This holds also for a series of compounds, since in the crystals of the compounds, the distribution of both kinds of atoms is always normal. In temperature ranges with no diffusion, there are two principal cases to be differentiated for the relation of the potential to the composition.

1. The potential of the compound A_mB_n differs slightly from that of the nobler component, the crystals A_mB_n behave chemically as the nobler component. In this case the potential will decrease practically to that of the more noble component B at the composition A_mB_n , at

the same time the less noble component disappears from the crystal conglomerate. (Fig. 225.)

2. The potential of the compound A_mB_n differs slightly from the less noble component. Then with increasing content of B the potential falls only a little with the disappearance of the A crystals. (Fig. 226.)

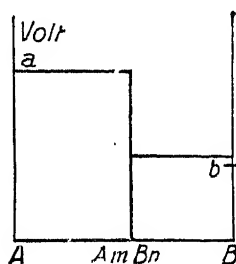


FIG. 225

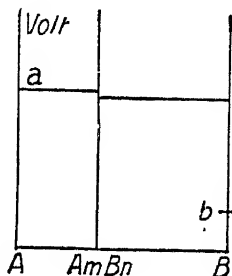


FIG. 226

In the first case the sudden decrease of the potential may be easily recognized. In this case if the microstructure of the alloy series is not known there remains a doubt whether we are dealing here with the disappearance of the crystal species A and the occurrence of B, or with a resistance limit of a solid solution series. In the second

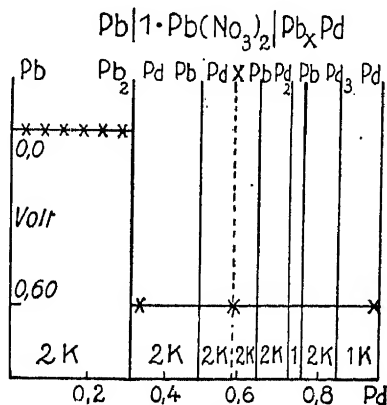


FIG. 227

case the decrease of potential at $A_m B_n$ may be easily overlooked if its amount does not exceed the error of determination. The establishment of the potential lines is therefore no certain means for investigating the microstructure of an alloy although it has been many times recommended. Examples of this are—

1. The potential lines of the Pb Pd series determined by Puschin and Laschtschenko (*Z. anorg. Chem.* 62, 34 (1909)) (Fig. 227). The

potential of the alloy with Pd from 0.33 up is within the error of experiment equal to that of Pd against Pb. If the Pd content falls below 0.33 the potential of the alloys against lead falls to the zero value since Pb crystals occur. The microstructure of this series of alloys has been established by Ruer (*Z. anorg. Chem.* 52, 345 (1907)). The solid solution series of 1.0 to 0.87 Pd is followed by a second from 0.80 to 0.75 mole Pd whose end member corresponds to PbPd_3 . There follows the following singular crystal series PbPd_2 , Pb_3Pd_4 , PbPd and finally Pb_2Pd . All these crystal species have potentials that, within the error of experiment, do not differ from that of Pd against Pb.

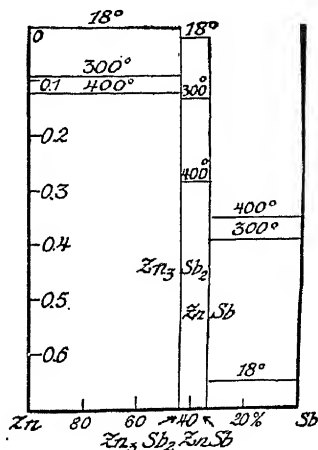


FIG. 228

2. The compound Cd_3Sb_2 according to R. Kremann (*Z. Metallk.* 2, 24 (1920)) shows a potential of 0.20 volt against Cd, while the potential of the compound CdSb lies between that of Cd and Sb and is coincident with that of the hydrogen electrode.

3. The compounds Zn_3Sb_2 and ZnSb are similar. At ordinary temperature the compound Zn_3Sb_2 is only 0.04 volt more noble than Zn and the compound ZnSb behaves as Sb since it does not dissolve in HCl any more rapidly than Sb while the compound Zn_3Sb_2 is easily dissolved. At high temperatures the compound Zn_3Sb_2 is markedly more noble than zinc and the compound ZnSb less noble than antimony. At higher temperatures the difference of potential between ZnSb and Sb increases as does that of Zn_3Sb_2 against Zn. This is shown in Fig. 228. With the occurrence of diffusion the real potentials of the compounds are observed.

At high temperatures where there is a sufficient movement of the atoms in the crystals of an alloy series the potential concentration lines must be greatly changed. Immediately the independence of the potential on the content of the less noble metal disappears the potential of

the nobler metal against the less noble falls greatly with small additions of the noble component. As a result the potential changes on the disappearance of a species of crystal already present and the appearance of a new crystal are not very marked corresponding to the generally small affinity of two metals in their compounds. In this temperature range the potential lines follow the rules of the equilibrium theory.

(e) The occurrence of charges with foreign ions. If the solid body whose surface is to be investigated is a metallic conductor we need only to connect it with one pair of quadrants of an electrometer and the other pair and a comparison electrode to the earth. If the body and the electrode are immersed in an electrolyte the observed potential corresponds to the cation present on the surface of the body. For example if PbS or Mn₂Si are immersed in H₂SO₄, they will show if they have been exposed to damp air, not the Pb or Mn potential but rather the hydrogen potential. On the surface, a cation interchange with the electrolyte has taken place, the less noble metal has precipitated the nobler hydrogen ions. Freshly molten PbS or Mn₂Si show in solutions of Pb or Mn salts the potential of Pb or Mn, they however become nobler with time and show after a time the H potential. (*Z. anorg. Chem.* 113, 149 (1920).)

The alloys of Au, Ag and Cu with less noble metals do not show such hydrogen adsorption but those of Sb, Si, S and Se do. This hydrogen adsorption may be easily replaced by Cu, Ag and Au. Apparently this cation interchange only affects the outer layer of atoms. Therefore the anions in the lattice appear to be tightly connected and the cations appear to be held only by electrical forces.

11. Diffusion of two Metals by Cathodic Polarization (Tammann, u. Wiederholt, *Zeitschr. f. anorg. u. allg. Chem.* 125, 1 (1920)).

By observing the potential existing between two metals immersed in a solution of the less noble metal after breaking a short circuit across the cell, we may follow the retention of polarization of the noble electrode and study the conditions which affect this process.

In Fig. 229 the potential π of a cell Zn | 0.5 mole. ZnSO₄ | Ag is plotted in relation to the time t after breaking a short circuit of 65 minutes duration. If π is plotted in relation to $\log t$, the curve $\pi = f(t)$ is resolved into three straight lines ab , bc , and cd . Each of these lines is expressed by an equation of the following form

$$\pi = \pi_1 + \frac{\pi_1}{\ln a_1} \ln t. \quad (1)$$

Here π_1 and $\ln a_1$ are the intersections of the lines on the two axes of the coordinate systems.

Each of the three lines corresponds to an e -function of the form

$$a_1 e^{\frac{\pi - \pi_1}{\pi_1}} = t. \quad (2)$$

The recovery curves of a metal after cathodic polarization, the function $\pi = f(t)$, can in general be expressed by three e -functions whose corresponding curves intersect in the points b and c (Fig. 229). The constants of the equation (2) are different for the three portions of the curve.

The constants of portions 1 and 2 are to a considerable degree dependent on external conditions of the polarization. For the first line they are dependent on the oxygen content of the electrolyte and especially on the oxygen concentration of the metal. Since these

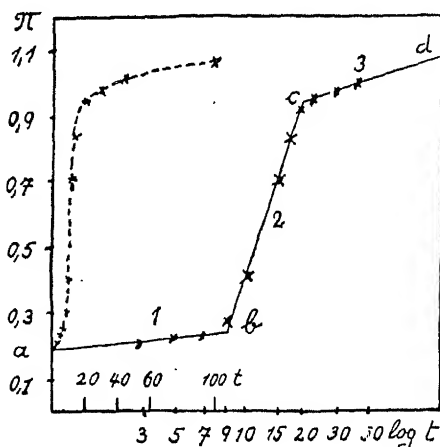


FIG. 229

variables cannot be determined in other ways, parts 1 and 2 of the recovery curve are not of particular interest. On the other hand the direction of the third logarithmic curve is independent of external conditions, but is determined by the nature of the electrode and the polarizing cation.

By short-circuiting a cell, the ions of the less noble metal discharge on the noble, however a layer of the pure base metal is not formed, since on the precipitation of the first trace of base metal, the potential would fall to zero. The noble metal must therefore diffuse into the precipitated base metal. The changes in the cathode with which we are dealing here are not visible.

If we extrapolate by means of the first logarithmic line $\pi = \pi_1 + \frac{\pi_1}{\ln a_1} \log(t + 1)$ to the potential value for $t = 0$, we obtain after ten minutes of short circuiting, a value of $\pi_{t=0}$, which is 0.03 to 0.58 volts

more noble than the base metal and which as a rule decreases with the time of short circuiting.

At the moment of breaking the short circuit there accordingly exists at the cathode a potential which is appreciably different from that of the base metal. This final condition is characterized by the fact that the amount of base metal precipitated is greater than that dissolved by the electrolyte whereby the further thickening of the layer of base metal is prevented. It would however come to a standstill at once if the noble metal did not diffuse and thereby increase the potential difference of the two electrodes. The potential difference of a short circuited cell is accordingly a complex function of the duration of the short circuit.

After opening the short circuit when the amount of precipitated metal is large, the recovery of the cathode takes place along the first logarithmic line, whereby the base metal goes into solution and the noble metal on the surface in the base metal is reached. No matter whether mutual diffusion between the noble cathode and the base precipitate has taken place, the amount of metal over the original surface of the cathode is very small, therefore the concentration of both metals is greatly changed as soon as the original surface is reached by oxidation of the precipitated layer. Then the same amount of oxygen brought to the cathode will cause a much greater potential change than before and correspondingly the constant $\frac{\pi_1}{\log a_1}$ will alter rapidly, so rapidly that its change appears discontinuous if the determination of π is not made at very small intervals of time.

Also in the second part of the recovery curve, external conditions are of great influence, which causes us to conclude that we are dealing with a layer that still does not lie within the noble metal but is essentially a layer on the surface of the noble metal, which has diffused the base metal mixed with small amounts of the base metal.

Finally the last part of the recovery curve, the third logarithmic line is independent of the oxygen content of the electrolyte. Here the oxygen concentration is sufficient to oxidize at once any metal diffused from the noble metal into the electrolyte, the increase of potential is accordingly determined by the diffusion velocity of the base metal out of the noble metal.

12. The Stainless Steels.

Upon the immersing of iron in concentrated nitric acid or by the anodic polarization in a solution of sulfuric acid it loses the ability to precipitate Cu or Ag out of their solutions. This passive condition of iron however is transient. On the other hand chromium prepared aluminothermically becomes spontaneously passive. In dilute hydrochloric acid especially on heating, Fe and Cr are both active and dissolve with evolution of hydrogen, also by cathodic polarization both

metals can be made active. However while Fe remains active after this treatment and oxidizes in water, Cr becomes spontaneously passive. It would be expected that in the solid solutions of Fe with Cr which form up to 30 per cent. Cr that the Cr when present in a certain amount would impart to the iron the ability to become spontaneously passive—as to what this content is no a priori conclusions can be drawn. This content may be determined in the following way.

If we measure the potential changes in a chromium steel after cathodic polarization in 0.05 molar H_2SO_4 solution we find that steels with more than 15 per cent. Cr become spontaneously passive while those with less Cr remain active. By anodic polarization the Cr steels become somewhat more noble; this increased nobility decreases however with time and by cathodic polarization, immediately reaches its normal potential.

The final potentials after cathodic or anodic polarization measured against a hydrogen electrode are collected in the following table for several chromium steels (Sotter and Tammann, *Z. anorg. Chem.* 127, 200 (1923)).

Per Cent. Cr.	After Cathodic Polarization	After Anodic Polarization
0.....	— 0.25	— 0.27
10.....	— 0.29	— 0.30
15.....	— 0.27	— 0.27
20.....	+ 0.55	+ 0.58
30.....	+ 0.62	+ 0.57
40.....	+ 0.61	+ 0.58

Steels with 15 per cent. or less chromium are accordingly as base after anodic as after cathodic polarization while those with 20 per cent. and more become spontaneously noble after cathodic polarization.

Again it may be shown in other ways that chromium steels fall into two groups regarding their tendency to become passive. The steels containing less than 15 per cent. Cr dissolve on anodic polarization of less than 0.9 volt, but upon exceeding this potential they become passive. Steels with 20-40 per cent. allow only very little current to pass up to 2.1 volt. While the first series of chromium steels are active up to 0.9 volt and passive thereafter, the second is passive from the first and is similar to a Pt electrode.

It is claimed that another group of alloys which besides chromium contain principally Fe, Co or Ni are acid resistant, and like Pt are unattacked by strong nitric acid. In dilute hydrochloric acid they dissolve as do all passive metals. Actual true acid resistant alloys can only be prepared when a base metal forms a series of solid solutions with a noble metal, whose potential is more noble than hydrogen, then the action of hydrochloric acid takes place from 0 to $\frac{2}{8}$ or $\frac{4}{8}$ mole of the noble metal. While in this case we are dealing with a stable protective action of the noble metal with passive alloys, only the sur-

face is protected by a loosely bound layer of oxygen. Hence the instability of the passive state is readily understood. The protecting layer of oxygen is easily removed by hydrogen ions obtained by cathodic polarization or the action of dilute hydrochloric acid. With Cr this protecting layer forms spontaneously in water or air while active iron rusts, since the protecting layer does not form and the iron decomposes water with the formation of $\text{Fe}(\text{OH})_2 \longrightarrow \text{Fe}(\text{OH})_3$ and hydrogen.

Summary

The chemical equilibrium theory may only be employed with the restriction that in all parts of the system, the molecules undergo un-oriented motion. Thereby the concentration in not too small regions is determined for each part of the system. Alloys (solid solutions and compounds) with the exception of amalgams do not fulfill these conditions at ordinary temperatures, since there is no appreciable freedom of the molecules, nevertheless the molecules or atoms vibrate about equilibrium positions and their reaction velocity is still considerable. At still lower temperatures the reaction velocity also vanishes. In the intermediate zone lies the usefulness of the atomistics of the reactions of binary mixtures in the isotropic or anisotropic state, since in this field during the disintegration of isotropic phases, the concentration at the surface is not changed, while in the disintegration of anisotropic phases with normal distribution the greatest variations occur.

In the temperature range where no freedom of the atoms exists the chemical and galvanic properties on the one hand and the physical on the other hand are essentially different in their relation to the composition of the solid solution. While only discontinuous changes of the chemical and galvanic properties occur in this temperature range, the physical properties change continuously. Such a continuous change is found for the relation of the volume, the elastic properties, the electrical conductivity, the heat conductivity and the magnetic permeability to the composition. For the relation of the thermoforces of solid solutions, W. Geibel (*Z. f. anorg. Chem.* 69, 38 (1911) and 70, 240 (1911)) and G. Borelius (*Ann. d. Phys.* 53, 615 (1917)) have found continuous curves and also straight lines that intersect at compositions corresponding to multiple proportions. This reminds us of the discovery of L. Hollman (*Z. f. phys. Chem.* 3, 195 (1901)) that the vapor pressure isotherms of the solid solutions of alums and vitriols had two marked minima. Between these minima were points in which these curves always intersected at compositions corresponding to multiple proportions.

The relation of the physical properties of the solid solutions to their compositions cannot be used to determine the constitution of the solid solution, i.e. the kind of distribution of its atoms in the space lattice.

On the other hand the relationship of chemical properties allows conclusions to be drawn regarding the atom distribution.

The conditions here are entirely similar to those with the carbon compounds. On the basis of their physical properties alone as e.g. the molecular refraction or the molecular volume, it is hardly possible to determine their constitution. On the other hand from their decomposition through different reactions their constitution may be determined on the basic assumption that within each decomposition product, no rearrangement of the atoms in the molecules took place. With both carbon compounds and solid solution series, the temperature range in which there is no freedom of the atoms in the molecules or in the lattice but in which reactions will still take place is quite narrow.

III. THREE COMPONENT SYSTEMS

The theory of three component systems has been developed by Roozeboom and Schreinemakers along the lines laid down by Gibbs. Schreinemakers especially (*Z. f. phys. Chem.* 50, 169 (1905); 51, 547 (1905); 52, 513 (1905) and *Die Heterogenen Gleichgewichte* by Roozeboom, III, and *Die Ternären Gleichgewichte* by Schreinemakers) has devoted his attention to the explanation of the frequent complex relations existing here. We will not attempt here to develop the theory of three component systems but will discuss only a few of the frequent examples occurring in this field.

The practical art of alloying has made only a little use of the theory of three component systems, although a series of problems have come up whose solution would be of use in practice. It is frequently of practical interest to determine which composition of a ternary mixture has the lowest melting point or the question arises at which composition in a ternary solid solution series is a maximum of any given property such as the electrical resistance, ductility or tensile strength. Without a knowledge of the elements of the theory of three component systems these questions are very difficult to answer. In any case much unnecessary work may be avoided if the problem is surveyed on the basis of theory and not attacked by purely empirical methods.

The number of three component systems which have so far been investigated is not large. The rarity of ternary compounds may accordingly be the cause of the delay in studying the systems. In the equilibrium diagrams of ternary metallic systems so far investigated, there have been determined for the most part only the limits of miscibility in the isotropic and anisotropic states. Also, of the three component systems which form the basis of the petrography of the future the only ones which have been so far investigated are Al_2O_3 - CaO - SiO_2 and Al_2O_3 - Na_2O - SiO_2 .

1. The Graphic Representation of the Composition of a Ternary Mixture.

If all possible mixtures are to be considered in representing the composition, the surface of an equilateral triangle may be appropriately selected for plotting the concentrations, every point therein representing a definite ternary mixture. The pure components A, B and C correspond to the corners of the triangle, to the sides of the equilateral triangle to the three binary series, AB, AC, and BC, and to the points in

the triangular plane itself, the ternary mixtures. (Fig. 230.) (If we wish to represent only mixtures which are rich in a single component, e.g. A, the amounts of B and C are calculated to a constant amount of A. The amounts of B or C may then be plotted on one of the two axes of a right angled coördinate system. The mixtures which contain B and C are represented by points in the coördinate plane.)

The representation of the composition on an equilateral triangle is based on the following two properties of such a triangle:

1. The sum of the distance of every point in an equilateral triangle from the three sides is equal to the height.

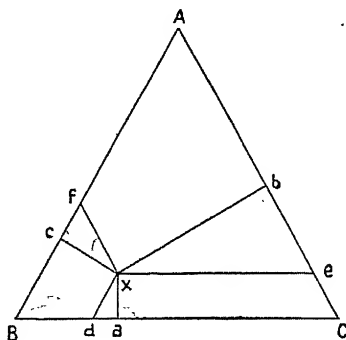


FIG. 230

2. If parallels to the three sides are drawn through a point x in an equilateral triangle the sum of the portions xd , xe and xf is equal to one side of the triangle (Fig. 231) and since the three right triangles axd , dxe and $cx f$ are similar the following relation holds: $xa : xb : xc = xd : xe : xf$.

To find the point corresponding to a given composition of a ternary mixture is easily accomplished. Let the percentage contents of the mixture in A, B and C be p , q and r . All mixtures with p per cent. A lie on a parallel to the side opposite A, or BC. This parallel cuts from all the lines going out from A, the portion $\frac{p}{100}$. For the mixtures with q per cent. B as well as r per cent. C we obtain the corresponding parallels to AC and AB respectively. The three parallels intersect at a point which corresponds to the given composition of the mixture.

If the three sides of the triangle are each divided into 100 parts and three groups of parallels passed through the division points, the point which corresponds to a given composition in weight or atomic per cent. can be obtained at once. The parallels are counted off corresponding to the percentages of the individual components from the points of the pure components to the opposite side. The counting off for two components is sufficient, the intersection of the parallels ob-

tained in this way gives the desired point. The counting off of the parallel for the third component can serve as a check on the first two countings; the third parallel must go through the intersection of the other two.

Two sections in the triangle are of special significance; along a section parallel to one of the three sides the content of the component which lies on the opposite side is constant. Along a line which passes through a corner of the triangle, the ratio of the amounts of the two components through the corners of which the line does not pass is constant. When one of the components separates out of the mixture in the pure state as a gas, liquid or crystal, the composition of the remaining mixture must vary along a line which goes through the composition point of the mixture and the corner of the separating component. The point which represents the composition of the remaining mixture is thereby moved forward away from the corner of the triangle under consideration.

2. Crystallization in Ternary Systems.

(a) The three components form with each other neither compounds nor solid solutions and are miscible in all proportions in the liquid state. If the equilibrium temperatures are projected vertically to the concentration plane, the temperatures at which one kind of crystals is in equilibrium lie on a plane which sinks from the melting point of the crystal under consideration to lower temperatures. To each of the three components corresponds such a plane on which the crystals of each component are in equilibrium with a series of ternary melts. Each two of these three surfaces of the beginning of crystallization intersect in a space curve along which the two kinds of crystals are in equilibrium with a series of ternary melts. These three space curves obviously start from the three eutectic points of the three binary systems and finally intersect at a temperature that lies below the lowest binary eutectic point. At this point the crystals of the three components are in equilibrium with a melt. This melt is accordingly saturated with all three kinds of crystals and as a result of this, crystallizes completely at constant temperature.

Fig. 231 gives a view of the space model from which we can read off the course of crystallization of the various mixtures. The projection of the points of the space model on the triangular plane gives the composition of the phases under consideration. They are designated with corresponding letters with the addition of a prime for a distinguishing mark.

The crystallization of a melt whose composition is α' , will begin at the point α with the separation of A crystals, if no supercooling occurs. As a result, the melt becomes poorer in A and its composition varies along a line through the point A' and α' from α' to β' . The temperature changes along the space curve $\alpha\beta$, the intersection of the surface drop of primary precipitation of A with a plane which

ditions is greatest for the melt o and decreases proportionally to the distance from o , disappearing at the sides of the triangle. The time of the eutectic crystallization is proportional to the distance of the points of the plane of a tetrahedron from its basal plane, the plane of the equilateral triangle abc (Fig. 231 lower part). The vertex of the tetrahedron (o) lies vertically below the eutectic point o .

Concerning the relation of the temperature of the second arrest on the cooling curves to the composition of the melts we may say the following.

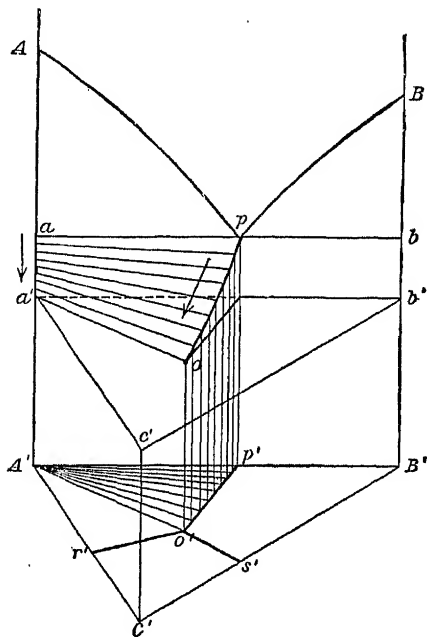


FIG. 232

All melts from which the same kind of crystals primarily precipitate and whose compositions lie on the same straight line that goes through a corner of the concentration triangle that represents the pure crystal under consideration (e.g. line $A'\beta'$ Fig. 231) will have the second arrest at the same temperature. Fig. 232 explains this proposition. The surfaces of the beginning of crystallization are here left out, and of the space curves along which two kinds of crystal are in equilibrium with a melt, only the curve po is shown; its projection on the plane of the concentration triangle $A'B'C'$ is the curve $p'o'$. The melt whose composition falls within the partial triangle $A'o'p'$ and which on the straight lines through A' reach by precipitation of A the same composition at the intersection of the lines with $o'p'$. As a result

this, the first crystals of B form at the same temperature from all the melts if supercooling is excluded. This secondary crystallization in a mixture, whose original composition is in the small triangle $A'o'p'$, occurs on a surface that results in the following way. If a line, which touches the line aa' and the curve po , glides parallel to the triangular plane $A'B'C'$, we obtain the surface of secondary crystallization $apoa'$. There are six such surfaces. The two end points of the gliding lines which develop the surface give the two phases that are in equilibrium on it.

We can now easily see, how the temperature of the second arrest on the cooling curve, changes in relation to the composition. If the

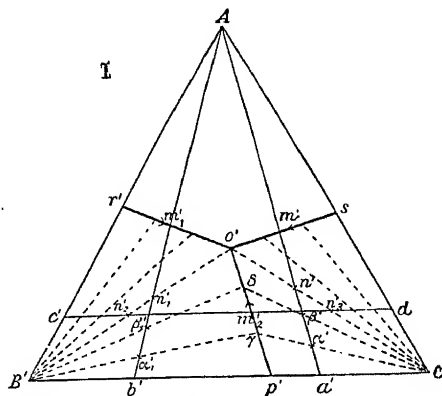


FIG. 233

composition exceeds the boundaries of one of the six small triangles, over each of which lies a surface of secondary crystallization, a sudden change in the course of the curve of secondary crystallization occurs. For example, in a section parallel to $A'B'$, between o' and $A'B'$, the temperature of secondary crystallization first falls with increasing content of B , after passing $A'o'$ it increases, after passing $o'p'$ it again falls and finally, after passing the line $B'o'$, increases again. On the basis of this accurate description of the course of crystallization in ternary melts for the separation of pure components, Sahmen and von Vegesack (*Z. physik. Chem.* 59, 251 (1907)) have solved the problem of finding the ternary eutectic point, by determining the smallest possible number of sectional diagrams.

For this purpose, only a diagram of a section parallel to one of the triangle sides, or the diagrams of two sections going through a corner of the triangle, need be determined.

In Fig. 233, the parallel $c'd'$ to the triangle side $B'C'$ designates the section, whose diagram is given in Fig. 234. The two curves for the beginning of crystallization cm_2 and dm_2 , must intersect on the

space curve of the equilibrium, between two kinds of crystals and the melt, at the concentration m_2' .

From m_2 , two curves of secondary crystallization go to lower temperatures. The eutectic temperature is reached by them at o_3 and o_4 , which correspond to the concentrations n_2' and n_3' . The cooling curves of melts of this concentration lack the arrests of secondary crystallization.

In the sectional diagram Fig. 234, the curve of secondary crystallization consists of four branches. The intersection o_3 and o_4 of each two of these branches must lie vertically over the line $B'o'$ and $C'o'$, and above the intersection points of these two lines with the parallel $c'd'$ (Fig. 233). These intersections correspond to the concentration n_2'

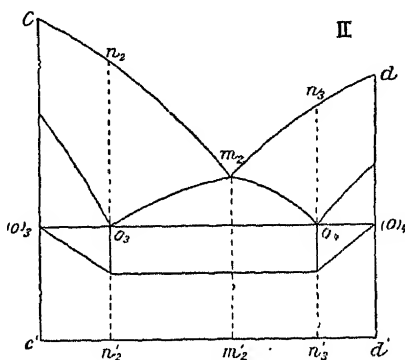


FIG. 234

and n_3' . Only the melts n_2' and n_3' may assume the composition of o after precipitation of B or C (without secondary crystallization of the second pure component) since n_2' and n_3' lie on the line $B'o'$ and $C'o'$. Accordingly, if the cooling curves of eight melts are determined, of which, two each lie right and left of the point o_3 and o_4 , the intersection of the curves with their second arrests, o_3 and o_4 may be found (Fig. 234). If the appropriate concentrations n_2' and n_3' are introduced into the diagram of Fig. 233 and a line passed through B' and n_2' as well as through C' and n_3' these lines will intersect in the sought ternary eutectic point. The durations of the eutectic crystallization are proportional to the distances of the three sides of the trapezium above the lines (o_3) o_3 , o_4 (o_4) (Fig. 234); the points o_3 and o_4 may accordingly be determined by determination of the durations.

For finding the ternary eutectic point o' , the determination of two diagram sections may be made, whose sections pass through the point A (Fig. 233) and the opposite side of the triangle $B'C'$ on opposite sides of the binary eutectic point p' .

The two diagram sections have the form of Fig. 235 and Fig. 236. The temperature of the beginning of secondary crystallization is the

same for all melts on the line Am' (Fig. 234) and the same also holds for the melts along the line Am_1' . From the point m_1' , the temperature of beginning of crystallization falls with decreasing content of A to the temperature of the ternary eutectic, which is reached at point n_1' . By further decrease of A, the temperature of secondary crystallization again increases. The composition n_1' of the point o_2 (Fig. 236) and n' of point o' (Fig. 236) may accordingly be determined from the two diagram sections, either by determining the intersection of the two curves of secondary crystallization, or by determining the time of the eutectic crystallization, whose greatest duration in the two diagram sections corresponds to the points o_2 and o_1 respectively. If n_1' and n'

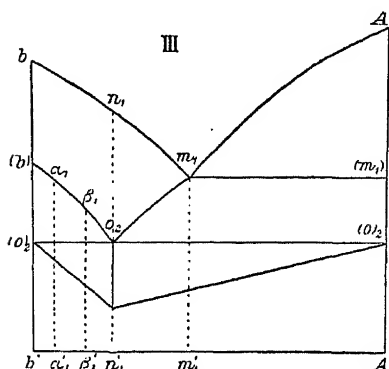


FIG. 235

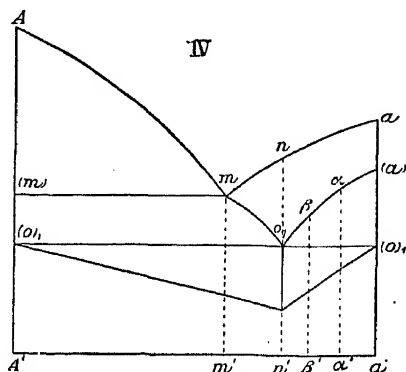


FIG. 236

are introduced in Fig. 233 and a line drawn through n_1' and B' and also through n' and C' these two will intersect at the point o .

After determining the position of the ternary eutectic point o' , the course of the space curve of secondary crystallization op or its projection $o'p'$ (Fig. 233) may be obtained from the diagrammatic section Figs. 235 and 236, or a part of its course from the diagrammatic section Fig. 234. It must be borne in mind that the planes which intersect the equilateral triangle normally in the lines $B'\gamma$ and $C'\gamma$ (Fig. 233), cut the surface of crystallization in two lines, that run their course at the same temperature (see Fig. 232). As a result we need only two points at the same temperature on the curves for secondary crystallization $(b) o_2$ and $(a) o_1$ (Figs. 235 and 236), whose concentrations α_1' and α' are in the triangle $A'B'C'$ (Fig. 233). If we draw lines through β' and α_1' as well as through C' and α' , their intersection γ is a point on the projection $o'p'$ of the space curve op .

For a complete determination of the space curves op , os , and or it is necessary to establish three such sets of two diagram sections. Each pair of sections must cut the opposite side of the triangle on different sides of the binary eutectic. Still all six diagram sections are not needed in their entirety.

(b) Of the three components which are miscible in all proportions in the liquid state, two, A and B, form a binary compound D; solid solution formation does not take place. Three cases are to be distinguished from each other here: (1) the binary compound D melts in binary and ternary mixtures without decomposition, that

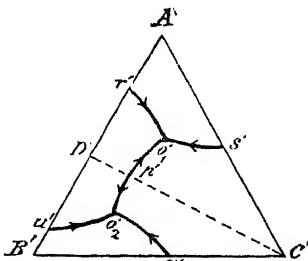


FIG. 237

is, without the precipitation of crystals of A or B; (2) this composition takes place in both binary and ternary mixtures by the melting of D, and (3) the decomposition does not take place in binary but in ternary mixtures within a certain concentration range.

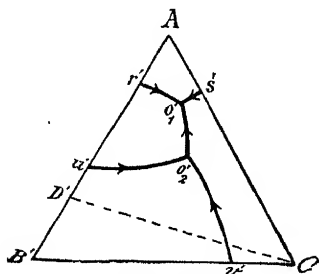


FIG. 238

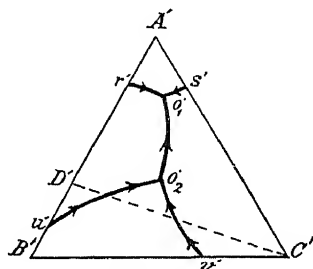


FIG. 239

Since in all these cases four kinds of crystals A, B, C, and D crystallize from the ternary mixtures, four surfaces of the beginning of crystallization will lie over the equilateral triangle $A'B'C'$, these surfaces will intersect in five space curves each corresponding to the equilibrium of two kinds of crystals with a series of ternary melts. In Figs. 237, 238, and 239 are shown the projections of these space curves on the triangular plane $A'B'C'$. The arrows on the curves give the directions in which the temperature of the corresponding space curve falls.

The mixtures whose compositions lie on the lines through C' and D' may be prepared by mixing C and D. If now $D'C'$ runs inside the fields of primary crystallization of D and C, $u'o_2'o_1'r'$ and $v'o_2'o_1's'C'$ (Case 1, Fig. 237), all liquid mixtures on the line $o'C'$ will form conglomerates of D and C on crystallization. Crystallization takes

place in this section as in a two component system where the two substances crystallize in the pure state.

If however $C'D'$ does not traverse the field of primary crystallization of D (Case 2, Fig. 238) or that of the crystal B in addition to it (Case 3, Fig. 239), B crystals will form out of at least part of the melts along the line $C'D'$, and will only later combine with the melt or with another kind of crystal to form the compound D. In the range in which $C'D'$ traverses the B-field D cannot melt without the precipitation of B.

If the binary compound D melts to a homogeneous melt of the same composition (Case 1, Fig. 237) it may be in equilibrium with a series of ternary melts at the same temperature. The solubility isotherms of D are semicircles whose center is at D' . Their tangential planes at the top are inclined to the triangular plane; their intersections with the planes of the two component systems are however parallel to the sides of the triangle. The temperature concentration plane which in $A'B'$ is vertical to the triangular plane cuts off a part of the summits.

The triangle $A'B'C'$ is divided into two parts by the line $D'C'$. In each of these parts of the triangle lies a ternary eutectic point o_1' and o_2' , and crystallization takes place in both of these partial triangles exactly as in the case where the pure components crystallize from the ternary melts.

If as in Fig. 238, $D'C'$ does not intersect the field of primary crystallization of D, as soon as the melt reaches the space curve $u'o_2'$ due to the primary precipitation of B, these primary precipitated B crystals form the compound D with their melt. With falling temperature this reaction continues till the melt has the composition o_2' , then the rest of B is transformed into the two kinds of crystals D and C. The temperature of this reaction is however not a minimum temperature. After B has disappeared the temperature falls further to the point o_1' where D and C crystallize simultaneously. Finally the remainder of the melt o_1' crystallizes at the temperature of o_1 , where the crystal A is added to the crystals of D and C.

If finally as in Fig. 239, $D'C'$ cuts the field of primary crystallization of D and also that of B, the compound D will melt without decomposition in a certain range of concentrations and in others with the precipitation of B crystals. On the other hand the compound D forms from B crystals and a series of melts along the space curve about $u'o_2'$, and out of the melt o_2' and B crystals D and C crystals again result. The end of the crystallization of all ternary melts takes place at the point o_1 .

(c) Of the three components miscible in the liquid state in all proportions, A and B form the compound D, A and C the compound E. Solid solutions do not occur. (v. Vegesack, *Z. anorg. Chem.* 54, 367 (1907).) Since under these conditions three eutectic points occur in the ternary mixtures at which the eutectic melts decom-

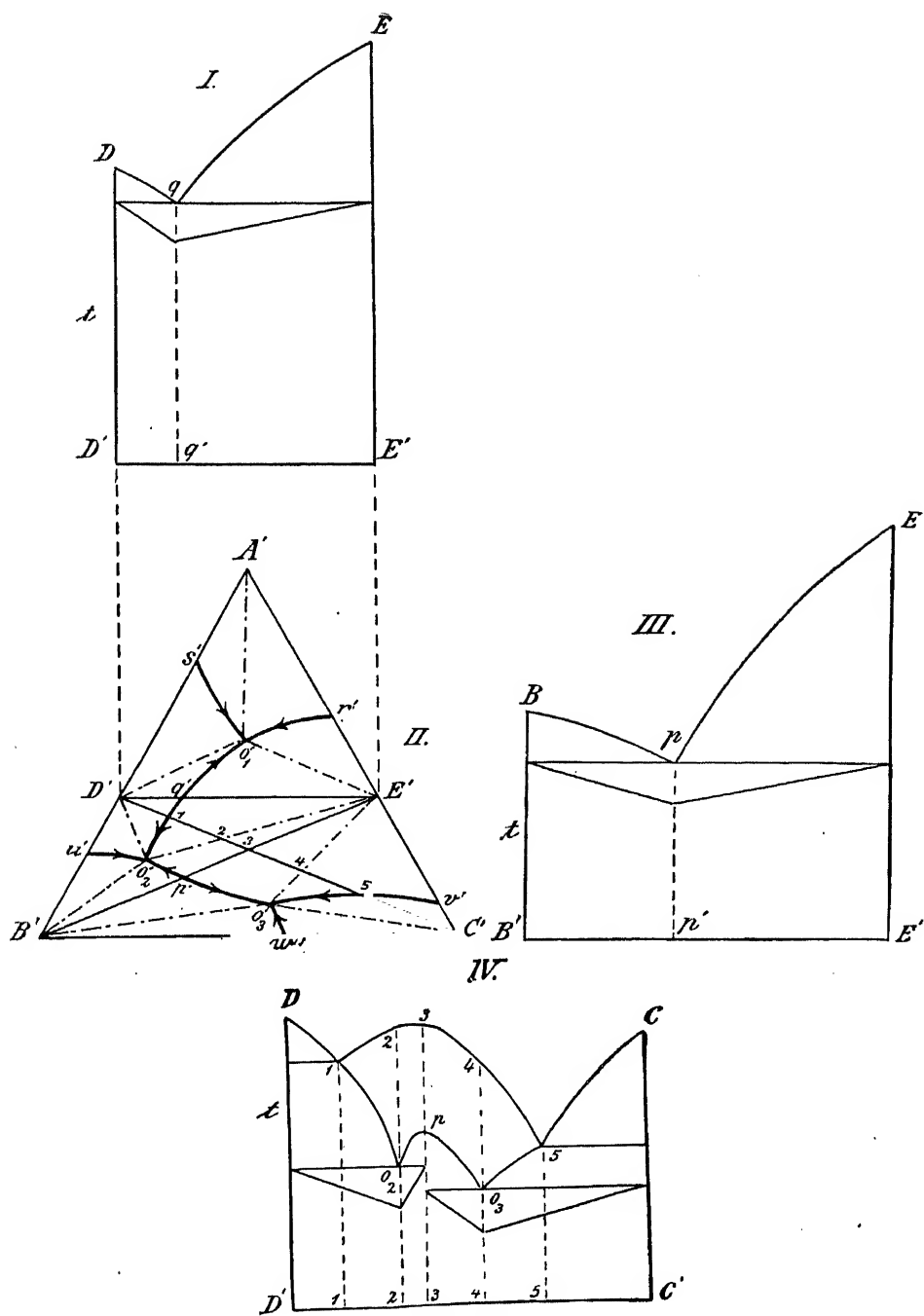


FIG. 240

pose on crystallization into three kinds of crystals we may divide the space diagram of the ternary system ABC into three prisms by two planes vertical to the plane of the equilateral triangle $A'B'C'$, each of which represents a simple ternary system with just three kinds of crystals. The triangle $A'D'E'$, Fig. 240 II, in which the eutectic point o_1' falls is determined by the decomposition of the binary compounds. Concerning the two other triangles however there are two possibilities. The two eutectic points o_2' and o_3' may lie on different sides of the trapezoid diagonal $B'E'$ or the diagonal $D'C'$. In the first case D, B and E crystallize at o_2' and B, E and C at o_3' . In the second case D, B and C crystallize at o_2' and D, E and C at o_3' . In the first case o_2' o_3' is the projection of the equilibrium curve of B and E with a series of melts and in the second case that of D and C. In the first case the section $B'E'$ Fig. 240 III has the properties of a simple binary system, while the section $D'C'$ Fig. 240 IV is composed of two sectional diagrams of simple ternary systems. In the second case the section $D'C'$ has the properties of a simple binary system and the section $B'E'$ is composed of two sectional diagrams of simple ternary systems.

If we conceive of the point o_3' in Fig. 240 II as being so far displaced that it falls into the triangle $D'E'B'$ whereby the curves $v'o_3'$, $w'o_3'$ and $o_2'o_3'$ must follow the motion of o_3' and hence the space curve over $o_2'o_3'$ which possesses a maximum over the intersection of $o_2'o_3'$ with $B'E'$ loses this maximum. From this the temperature may constantly fall from point o_3 to point o_2 . The melt o_3' may no longer break down into B E and C but from B and E at the point o_3 the melt o_3' and C result with absorption of heat. The compound E' accordingly melts with decomposition in a part of the ternary system.

(d) The surface of crystallization of a ternary compound that melts to a homogeneous liquid. A binary compound which melts to a homogeneous liquid may only be in equilibrium with two binary melts of different compositions at a definite temperature. A ternary compound may be in equilibrium with a whole series of ternary melts at the same temperature. The compositions of these melts lie on a closed curve, or expressed otherwise the solubility isotherm of a ternary compound is represented by a closed curve. Inside of this curve lies the point representing the composition of the ternary compound. With falling temperature the distance of the solubility isotherms from this point increases in every direction. The surface of crystallization has accordingly the form of a dome. The tangential plane at the summit of this dome lies parallel to the triangular plane.

From these surfaces the surface of crystallization of a binary compound in a ternary system originates, while the surfaces of ternary compounds are displaced parallel till their summits fall in a plane which is normal to that of the sides of the triangle.

Ternary compounds are only known in such systems as form compounds in at least two of the three binary systems.

Roozeboom and Schreinemakers (*Z. f. phys. Chem.* 15, 588 (1894)) have established that in the ternary system H_2O , HCl and FeCl_3 a compound $\text{FeCl}_3 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$ occurs with a melting point of -3° , the solubility isotherm of this compound at -4.5° is a closed curve. However, since the surface of crystallization of the ternary compound is intersected by other surfaces it is frequently only partially formed.

Ternary metallic compounds appear rather seldom; up to now only the two, NaKHg_2 and NaCdHg found by E. Janecke (*Z. f. phys. Chem.* 57, 597 (1906)) and one $\text{Al}_6\text{Mg}_4\text{Cu}$ found by R. Vogel (*Z. f. phys. Chem.* 197, 265 (1916)) are known. The decomposition points of the first two lay on lines that pass through two binary compound points. NaKHg_2 lies on the line connecting the compound points NaHg and

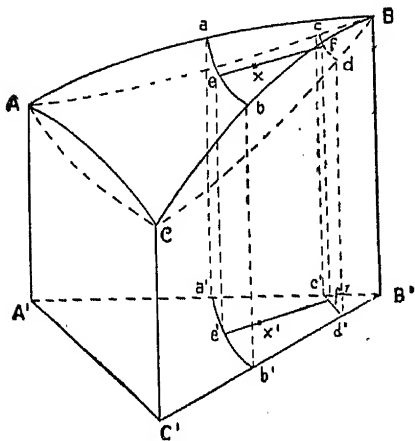


FIG. 241

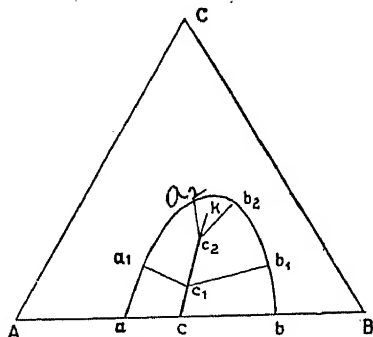


FIG. 242

KHg and NaCdHg lies on the line connecting the compound points NaHg_2 and NaCd_2 .

(e) The crystallization of solid solutions out of ternary mixtures. If in a ternary system the three binary systems form a continuous series of solid solutions it is apparent that in the ternary system no gaps in the miscibility will occur. The form of the surface for the beginning and the ending of crystallization may however be very different. It may have a minimum or a maximum or a point of inflection may occur.

Fig. 241 shows the surfaces of beginning and ending of crystallization for the case where no such singular points occur. For the three binary systems the curves for the beginning of crystallization are drawn full and those for the end are dotted. If a surface is passed through each of these the enclosed space is the space of the heterogeneous condition. A mixture of the composition x' whose temperature falls in this space decomposes into a melt and a solid solution whose composition is different from the total composition of the

Here also the curves cd , ab and ef refer not to one temperature but to the temperatures at which the two solid solutions are in equilibrium with a melt. The curves ab and ef therefore do not give the composition of the saturated solid solutions at ordinary temperature. As a rule the curves which show this differ only slightly from the curves ab and ef . If we assume an increase of the gap with falling temperature the ab will be correspondingly somewhat displaced, toward the line AC and the curve displaced toward the point B . The course of these curves is most certainly established by microscopic investigation of the conglomerates obtained. These must if their composition falls in the field $aefb$, consist of two components, while if it falls in field Bef or $ACba$ it will consist of only one component.

Finally if a miscibility gap occurs in all three binary systems whose

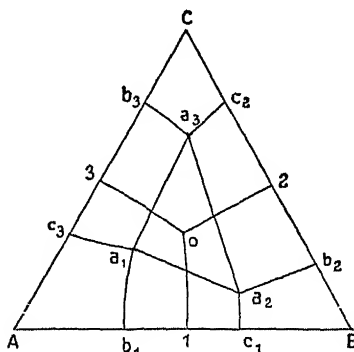


FIG. 244

boundary curves intersect, the number of different fields of existence of crystalline phases increases to seven. Fig. 244 gives a view of this. The conglomerates whose composition falls in the triangle $a_1a_2a_3$ consist of the three saturated solid solutions a_1 , a_2 and a_3 those whose composition falls in one of the three fields, $b_1c_1a_2a_1$, $b_2c_2a_3a_2$ and $b_3c_3a_1a_3$ out of two saturated solid solutions and those whose composition lies in one of the three fields, $Ab_1a_1c_3$, $Bb_2a_2c_1$ and $Cb_3a_3c_3$ consist of only one kind of solid solution.

If the composition of the three saturated solid solutions a_1 , a_2 and a_3 is not appreciably influenced by the temperature the boundaries of the fields will not alter from the ordinary temperature to the eutectic temperature. By exceeding the eutectic temperature new phase fields occur in the triangle ABC ; that of the liquid mixture and the three fields in each of which a series of solid solutions is in equilibrium with a series of liquid mixtures. R. Salmen (*Z. f. phy. Chem.* 79, 421 (1912)) has given a comprehensive discussion of the course of crystallization in this case.

(f) Limited miscibility in the liquid state. If two liquids A

and B are not miscible in all proportions homogeneous mixtures can frequently be obtained by the addition of a third liquid C which is miscible in all proportions with A and B.

Two metals with slight reciprocal solubility are Zn and Pb. At 418° they are only relatively slightly soluble in one another. By the addition of liquid tin homogeneous mixtures may be obtained relatively rich in Pb and Zn. By cooling these mixtures lead and zinc rich alloys may be obtained which could not be obtained without the addition of Sn due to the slight miscibility of Pb and Zn, since at the beginning of crystallization the zinc layer holds only 1 per cent. of lead and the lead layer only 5 per cent. of Zn.

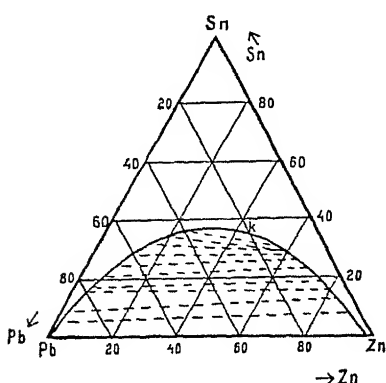
Miscibility Gap at 650°

FIG. 245

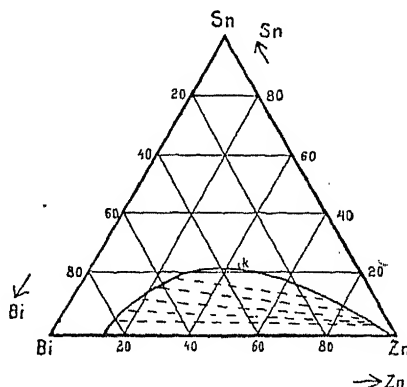
Miscibility Gap at 700°

FIG. 246

The knowledge of the influencing of the limits of the miscibility gap of two liquids by the addition of a third substance is accordingly of importance in the preparation of ternary alloys, two metals of which do not alloy.

Wright and Thompson have determined the limits of the miscibility gap of Zn and Pb for additions of Sn (*Proc. Roy. Soc.*, London, 45, 461 (1889)) and Ag (*Proc. Roy. Soc.*, London, 48, 25 (1891)) and that of Zn and Bi for additions of Sn (*Proc. Roy. Soc.*, London, 49, 156 (1891)). Fig. 245 gives the results of these determinations at about 650° for Zn, Pb, Sn, and Fig. 246 those for Zn, Bi, Sn at 700° .

The dotted lines connect the composition points of two liquid layers which are in equilibrium with each other at the same temperature. At the point k the composition of the two layers is identical. The point k need not fall on the tangent point of a parallel to the Pb-Zn or Bi-Zn axis to the boundary curve of the miscibility gap.

The area of the miscibility gap as a rule diminishes with rising temperature. The boundary surface ends finally in the form of a

dome whose summit lies over the plane of the equilateral triangle or over the side of the same. If the latter is the case the temperature of complete miscibility is the highest for a binary mixture in the other case for a ternary mixture.

If in two binary systems miscibility gaps in the liquid state occur the miscibility interval in the ternary system may have the form of a band which connects the two gaps of the binary systems. With rising temperature a constriction of the band forms which breaks up the band into two parts, both of these parts may close in the way described.

If there is a miscibility gap in all three binary systems an equilibrium of three liquid layers may occur. As in Fig. 244 we have three fields of existence of homogeneous mixtures that lie in the three corners of the equilateral triangle, three fields of existence for mixtures of two liquid layers and in the center of the triangle $a_1a_2a_3$ the field

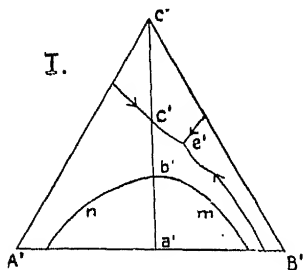


FIG. 247

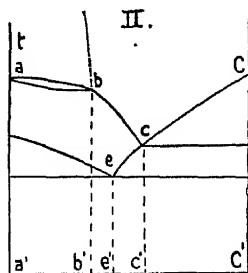


FIG. 248

for the mixture of three liquid layers. With rising temperature the fields of the homogeneous mixtures broaden at the expense of the other four fields. Thereby one of the fields of two liquid layers is decreased to the greatest extent. As soon as its boundaries against the fields of the homogeneous mixtures close to a curve the corresponding layer disappears from the equilibrium of the three liquid layers and therewith naturally the field $a_1a_2a_3$ of the three layers. Besides the miscibility gap bounded by a continuous curve one may exist as a band that disappears with rising temperature in the way described.

If only one miscibility gap is present in a three component system the crystals of the several components are in equilibrium with the two liquid layers at various temperatures, since the concentration of both layers changes with the total composition. The temperature-concentration points for the beginning and the end of this equilibrium lie on a ruled surface whose generation moves in space parallel to the triangular plane. In this case if we wish to get a general idea of the system by the examination of the fewest possible sections we will investigate those which go through the binary miscibility gaps lying over the sides of the triangle. Such a sectional diagram is shown in Fig. 248 for the case where the three components crystallize in the

pure state. The concentration of the break *b* on the curve for the beginning of crystallization of various sectional diagrams whose temperature has been determined gives two points on the boundary curve *m n* of the miscibility gap (Fig. 247). This boundary curve *m n* of the miscibility gap refers accordingly not to the same temperature and differs therein from the isotherm of the boundary curve Figs. 245 and 246.

3. Review of the Crystallization of Ternary and Quaternary Melts.

There are about thirty ternary and a few quaternary systems which have been investigated besides numerous investigations concerning ternary steels. The position of the surfaces of beginning and ending of crystallization as well as the boundaries of miscibility gaps of liquid mixtures and solid solution series have been approximately determined. Ternary metal compounds have not been found in the systems investigated; this may be due to the fact that the more comprehensive investigations have concerned metals with small tendency toward compound formation. With the metals that form numerous binary compounds as the alkali metals with Hg, Cd, Pb, or Sn ternary compounds are to be expected analogous to those found with FeCl_3 , which forms numerous compounds with H_2O and also a ternary compound with HCl and H_2O . In fact three ternary compounds NaKHg_2 , NaCdHg and $\text{Al}_3\text{Mg}_4\text{Cu}$ have been found and their number may well be considerably increased with the alkali metals.

The occurrence of a ternary compound introduces a new factor into a three component system which from the relations of the binary systems, the elements of the three component system, cannot be guessed. Since, however, ternary compounds occur so seldom we can on the basis of the three binary equilibrium diagrams make predictions concerning the course of crystallization in the ternary system. The experimental investigation then affords a closer check of this extrapolation from the three binary systems.

For the study of the relation of the properties of ternary conglomerates, as the volume, the electrical conductivity, the ductility, the tensile strength, etc., to the total composition, the determination of the miscibility gaps in the solid state is of great importance from what has been said concerning these relations in binary systems. The properties of alloys that consist of homogeneous solid solutions are represented by surfaces which may have maximum or minimum points, the properties of alloys with two kinds of crystals by ruled surfaces and that of conglomerates with three kinds of crystals by planes. If the boundaries of the fields of existence in the plane of the equilateral triangle are known, so are the boundaries of the surfaces, ruled surfaces and planes known which represent the properties in relation to the composition. Their intersection curves in space must fall together with the boundaries

of the fields of existence after projection on the plane of the equilateral triangle. In this sense the establishment of the fields of existence of ternary systems is not only of importance for the course of crystallization and the structure of the resulting conglomerates but is an important preliminary to the study of their physical properties.

In the following summary of the investigated ternary systems complete miscibility in the liquid state is designated f-. Ternary eutectics are designated by the letter E, their temperature and composition being given.

1. Low Melting Alloys

Sn Pb Bi f- E 96° 15.5 Sn 32 Pb 52.5 Bi Wt-Pct. (Charpy, *Contribution à l'étude des alliages* (1901), 203.)

Sn Pb Cd f- E 145° 57 Sn 21 Pb 22 Cd Atom. Pct. In the crystallized alloy heat evolutions occur at 118° and 112° whose amount decreases with increasing lead content. (Stoffel, *Z. anorg. Chem.* 53, 137 (1907).) The field of existence in which the primary lead containing Sn_4Cd crystallizes out of the ternary melt is not determined.

Sn Pb Zn. (Levi-Malvano and Ceccarelli, *Gazz. chim.* 41, 269 (1911).)

Sn Cd Bi f- E 103° 33.2 Sn 27.5 Cd 39.3 Bi Atom. Pct. (Stoffel l. c.)

Pb Cd Bi f- E 91.5° 40.2 Pb 8.1 Cd 51.6 Bi Wt-Pct. (Barlow, *Z. anorg. Chem.* 70, 178 (1911).)

Sn Pb Bi Cd f- E 70° 13.1 Sn 27.3 Pb 49.5 Bi 10.1 Cd Wt-Pct. (Parravano and Sirovich, *Gazz. Chim. Ital.* 42, 1 (1911).)

Sn Zn Cd f- E 163° 70.8 Sn 3.7 Zn 25.4 Cd Atom. Pct. (Lorenz and Plumbidge, *Z. anorg. Chem.* 83, 230 (1913).)

Sn Pb Sb f- E 189° 57.5 Sn 40 Pb 2.5 Sb Wt-Pct. Pb, SbSn containing Pb and Sn containing Sb were in equilibrium with these melts. Sb containing Sn also occurs at the surface of the beginning of crystallization of these three kinds of crystals. At 245° the Sb containing Sn, Sn Sb and Pb are in equilibrium with a melt that contains 80 Pb 10 Sn and 10 Sb. (Loebe, *Metallurgie* 8, 15 (1911); Campbell, l. c. 9, 422 (1912).)

Pb Cd Hg f- E practically pure Hg. The surfaces of beginning of crystallization of the three groups of solid solutions and their fields of existence have been determined. (Jänecke, *Z. physik. Chem.* 73, 328 (1910).)

Pb with additions of Na and Hg up to 6 per cent. (J. Goebel, *Z. anorg. Chem.* 106, 209 (1919).)

Pb with additions of Na and Sn up to 6 per cent. (ebenda).

2. Silver Containing Alloys

Ag Au Cu f- Au forms a continuous series of solid solutions with Cu and Ag. With Ag and Cu however there is a large gap. Accordingly there are two groups of alloys to be differentiated in the ternary

system, those which consist of homogeneous solid solutions and those which consist of two saturated ternary solid solutions rich in copper and silver, resp. (see p. 265). The point k lies at 42.5 Cu, 36.5 Ag and 21.0 Au and the composition of the solid solution with which this melt is in equilibrium is 42.5 Cu, 33.5 Ag, 24 Au (Atom. Pct.). (Jänecke, *Metallurgie* 8, 597 (1911).)

Ag Au Ni. (Cesaris, *Gazz. chim.* 43, 2, 609.)

Ag Sn Pb f- E 174° 1 Ag 63.4 Sn 35.6 Pb. The surface of beginning of crystallization of Ag-rich ternary solid solutions and the crystals of Ag_3Sn are strongly developed, those of the Sn and Pb form narrow strips. (Parravano, *Atti. Acc. d. Lincei* (5) 21, I, 575.)

Ag Sn Hg. (Huijet, *Journ. chem. Soc. Lond.* 103, 2247 (1913).)

Ag Zn Pb. The limits of the miscibility gap in the liquid state, which originates in the binary system Zn-Pb have been determined by numerous sections through the lead corner. (Kremann and Hofmeier, *Wiener Sitzungber.* 120, 2b, 283 (1911).)

Ag Cu Pb E 302° 2 Ag 0.5 Cu 97.5 Wt-Pct. The limits of the miscibility gap in the liquid state are not closely determined. The silver rich solid solutions contain a little lead, the copper rich more lead, the precipitated lead is practically Ag and Cu free. (Friedrich and Leroux, *Metallurgie* 4, 293 (1907).)

3. Magnesium Alloys

Mg Pb Sn f- Besides the two binary compounds SnMg_2 and PbMg_2 no compounds occur. The surface of beginning of crystallization of solid solutions rich in SnMg_2 is very strongly developed so that those of the four other kinds of crystals are of only small extent. In the section SnMg_2 - PbMg_2 the two saturated solid solutions have the composition 22 Mg 21 Sn 57 Pb and 19.3 Mg 1.2 Sn 79.5 Pb (Wt-Pct.). The crystals of SnMg_2 with the higher melting point take up considerably more PbMg_2 than the lower melting PbMg_2 take up of SnMg_2 . (v. Vegesack, *Z. anorg. Chem.* 54, 367 (1907).)

Mg Cd Zn f- E 250° 2 Mg 73 Cd 35 Zn (Atom. Pct.). (Bruni, Sandonnini and Quercigh, *Z. anorg. Chem.* 68, 73 (1910), 78, 273 (1912).)

4. Aluminum Alloys

Al Cu Mg Partial diagram Al Al_2Cu Al_3Mg . Ternary compound $\text{Al}_6\text{Mg}_4\text{Cu}$. (R. Vogel, *Z. anorg. Chem.* 107, 265 (1919), and W. Fraenkel, *Z. Metallkunde* 12, 225 (1920).)

5. Copper Alloys

Cu Sb Bi E practically pure Bi. Only two binary compounds Cu_3Sb and Cu_2Sb . In the section Cu_3Sb -Bi there is a miscibility gap in the liquid state. (Parravano and Viviani, *Gazz. chim. ital.* 40, II (1910).)

The diagrams Cu-Al, Cu-Sn and Cu-Zn are rather complex due to

the reactions which take place in the crystallized alloys. By the investigation of the ternary alloys the surface of crystallization has been fixed within certain limits and some data obtained concerning the structure of certain alloy series.

Cu Ni Zn f- E in the neighborhood of Zn. To this group belong nickel silver, argentan, etc. Besides these commercial alloys the alloys with 15-20 Ni, 73-80 Cu and 7 Zn are similar to Ag in color and ductility. The alloys with 33-40 Ni, 7-20 Cu and 40-52 Zn (Wt.-Pct.) are characterized by hardness and toughness. (Tafel, *Metallurgie* 5, 375, and 413 (1908).)

Cu Ni Ag (Cesaris, *Gazz. chim.* 43, 2, 365).

Cu Ni Pb (Parravano, *Gazz. chim.* 44, 2, 375).

Cu Ni Ag Au (Parravano, *Gazz. chim.* 44, 2, 279).

Cu Ni Co (Wahlert, *Osterr. Z. Berg. u. Huttenwesen* 62, 341).

Cu Zn Al (Levi-Malvano, *Gazz. chim. ital.* 41 II, 292; 42 I, 353 (1912). Jares, *Int. Z. Metallog.* 10, 1).

Cu Zn Pb (Parravano, *Gazz. chim.* 44, 2, 475).

Cu Al Sn (Andrew and Edwards, *Proc. Roy. Soc. London* 82, A 568).

Cu Sn Pt (Levi-Malvano, *Gazz. chim. ital.* 41 II, 297 (1911)).

Cu Sn Pb (Giolitti, *Gazz. chim. ital.* 40 I, 51 (1910)).

6. Alloys with Metals of the Iron Group

Fe Ni Cu f- The surfaces of beginning and end of crystallization as well as the course of the gap in the solid solution series Fe-Cu in the ternary system has been established (Vogel, *Z. anorg. Chem.* 67, 1 (1910)).

Fe Ni Mn f- Also in the crystal state there is miscibility in all proportions at high temperatures; at lower temperatures separation occurs due to reactions.

Fe Mn Cu f- The course of the gap in the solid solution series Fe-Cu in the ternary system is followed.

Ni Mn Cu f- miscible in all proportion in the crystal state at high temperatures; at lower temperatures separations as a result of transformations.

Fe Ni Mn Cu f- Sections of the tetrahedron of the four component system at constant Mn content have been investigated by Parravano, who has also investigated the three three-component systems. (*Gazz. chim. ital.* 42, 2 (1912).)

Further there have been numerous investigations of ternary steels. Guillet (*Les Aciers speciaux*, Paris (1905)). Portevin (*Revue de Metallurgie* (1909)). Fe-C-Mn, Goerens (*Metallurgie* 6, 538 (1909)). Fe-C-P, Wust, Goerens (*Metallurgie* 5, 73 and 561 (1908)). Fe-C-Sb, Fe-C-Sn, Goerens and Ellinger (*Metallurgie* 7, 72 and 76 (1910)). Fe-C-V, Putz (*Metallurgie* 3, 635 (1906)). Fe-Si-V, Vogel and Tammann (*Z. anorg. Chem.* 58, 76 (1908)). Fe-C-Si, Gontermann

(*Z. anorg. Chem.* 59, 373 (1908)), Fe-C-B Vogel and Tammann (*Z. anorg. u. allg. chem.* 123, 225 (1922)).

4. The Phase Rule.

A heterogeneous system (a mixture of substances of the same or different states of aggregation) consists of the parts; vapor, liquid layers and different kinds of crystals which can be separated by mechanical operations as filtering, picking out, etc. These parts are for chemically homogeneous bodies, one-component systems, identical with the states of aggregation.

To have a general expression the parts of a heterogeneous system are designated as phases.

The substances which are necessary for the preparation of all possible mixtures are called components.

The conditions for a determined equilibrium in a heterogeneous system are the following: The temperature and pressure must be the same in all phases and the concentration of the different components must be the same in every part of a given phase.

The system as such is determined by two series of variables

$$\begin{array}{llll} 1. & T, p & c_1' c_2' \dots & c_1'' c_2'' \dots & c_1''' c_2''' \dots \\ 2. & Q, v & m' & m'' & m''' \end{array}$$

T and p are the temperature and pressure, $c_1' c_2' \dots$ the concentrations of the components 1, 2 \dots in a phase, $c_1'' c_2'' \dots$ the same components in another phase, etc.

Q and v designate the heat content and the volume, and m', m'' the masses of the individual phases.

The change of mass of a phase, so long as the mass does not fall below a certain very small amount, is without influence on the variables of the first group. With changes of Q and v at constant total mass systems behave differently. In some the variables of the first group do not change if the heat content Q changes at constant pressure and the same holds for changes of volume v at constant temperature. These equilibria are designated as complete, those in which the variables of the first group change as incomplete. While by a change of a variable in the second group a change of a variable of the first group need not be brought about, the variables of the second group always change by a change in the variables of the first group.

As the degree of freedom F of a system in equilibrium is designated the number of variables of the first group which may be changed without a phase disappearing from the system.

According to J. W. Gibbs a relation exists between the number of phases r , the degrees of freedom of the system F and the number of components n . This relation is called the phase rule, and may be stated

$$F = n + 2 - r.$$

The proof of the phase rule can be arrived at most easily from the derivation given by F. Riecke (*Z. physik. Chem.* 6, 272 (1890)).

For each phase an equation holds through which its state is defined. These equations of state are of the form

$$\varphi(c_1' c_2' \dots p, T) = 0$$

where φ is the symbol of a certain function of the given independent variables. If in each phase all components occur the number of independent variables will be equal to the number of components plus 2.

If the number of phases r is equal to the number of independent variable, the system is clearly determined, since there are as many independent variables as equations of state. The system has accordingly no degrees of freedom if $n + 2 = r$ and the number of degrees of freedom is in general equal to $n + 2 - r$.

Heterogeneous systems may be classified and differentiated on the basis of their degrees of freedom. Corresponding to the number of degrees of freedom there are non-variant, uni-, tri- and multi-variant systems.

The use of the phase rule on one, two and three component systems is best illustrated by a geometric diagram of the equilibria.

One Component Systems

invariant	Such a system can only exist at a point p of
$F = 0 \quad n = 1 \quad r = 3$	the p, T plane, the triple point.
univariant	The points of this system lie on three p, T
$F = 1 \quad n = 1 \quad r = 2$	curves which intersect at the triple point.
divariant	The points in the fields of the p, T plane which
$F = 2 \quad n = 1 \quad r = 1$	are separated by the curves of the univariant equilibria represent the state of a homogeneous system.

Two Component Systems

invariant	The invariant system exists at a point of the
$F = 0 \quad n = 2 \quad r = 4$	c, p, T space, the quadruple point.
univariant	The points of this system lie on four space
$F = 1 \quad n = 2 \quad r = 3$	curves that intersect in the quadruple point.
divariant	The points lie on surfaces which divide the
$F = 2 \quad n = 2 \quad r = 2$	c, p, T space into regions of existence. The curves of intersection of these surfaces are the space curves of the univariant equilibria.
trivariant	The points of this system fall in the fields of
$F = 3 \quad n = 2 \quad r = 1$	existence.

For complete representation of the processes in three component systems with five variables three dimensional space is no longer sufficient. To obviate this difficulty the pressure is placed constant.

If the constant pressure is greater than the greatest vapor pres-

sure in the system we have with this representation of a system with three kinds of crystals and a liquid no degrees of freedom which is represented by a point in space. The equilibrium with three phases lies on a space curve, that with two on a surface and that with one in certain regions of existence.

Exceptions to the Phase Rule

1. The number of degrees of freedom of a system is not infrequently less than would be expected from the number of components and phases. This kind of limitation occurs only with many component systems. If in a many component system the number of phases $r = 2$ and the composition of both phases is the same the system has only one degree of freedom. Then we find at certain compositions maxima or minima on the equilibrium curves. These maxima or minima of the temperature concentration curves may remain unchanged by changing the pressure or may be shifted to other concentrations. The same holds for the maxima or minima of the pressure concentration curves on changes of the temperature.

In the equilibrium of vapor and liquid this displacement is shown in many cases.

It has been thought that the immovability of the maxima and minima were characteristics of chemical compounds. It is however possible that with chemical compounds such a motion may take place through the formation of solid solutions.

On the basis of phenomena that fall in the field of pure thermodynamics a characteristic for chemical compounds can naturally not be deduced. For this, facts must be drawn upon which allow of an atomistic explanation.

Such are to be sought in the characteristics of the phases of the concentration of the maxima and minima. If these correspond to the law of multiple proportions the phases may be considered as chemical compounds.

2. With the number of phases $r = 3$ still other restrictions may occur in three and multi-component systems in which the system has one, two or more less degrees of freedom than would be expected from the number of components. The conditions for this are that the system may be built up out of two definite phases of the system. By this condition the number of independent variables, namely the variable concentrations, are lessened one, two or more and hence also the number of degrees of freedom.

As an example a section of a three component system which combines the point of a ternary compound with the corner of the equilateral triangle, or the points of two ternary or two binary compounds or that of a ternary and a binary compound, will behave as a binary compound.

Similar limitations of the phase rule hold for multicomponent systems if the number of phases reaches that of the components.

3. There exist also cases where the number of degrees of freedom is more than would be expected from the number of phases and components.

These apparent restrictions are no longer noticed by sufficiently slow change of the heat content and the volume of the system. They do not accordingly occur with stringent fulfilling of the conditions of equilibrium.

If the change of a molecular species into one or more others requires a comparatively long time, for changes of normal velocity the system will have one more degree of freedom for each such reaction than would occur according to the number of phases and components.

The velocity of change of the heat content at which these restrictions of the phase rule are met is given by the condition that the concentration of the molecular species with the smallest velocity of transformation in any phase is dependent on its velocity of change of mass.

Cases where a one component system has the degree of freedom of a two component system have been investigated by Bancroft (*Journ. Phys. Chem.* 2, 143 (1898); 3, 72, 145, 551 (1899); 5, 182 (1901)), and Hollman (*Z. physik. Chem.* 43, 129 (1903)); see also Roozeboom and Aten (*Z. physik. Chem.* 53, 449 (1905)). A few binary alloys behave in their crystallization as three component systems. This behavior has been found by the author in the alloys of Al and Sb (*Z. anorg. Chem.* 48, 53 (1906)), of Fe and Cr (*Z. anorg. Chem.* 55, 402 (1907)) and also of Fe and Mo (*Z. anorg. Chem.* 55, 386 (1907)).

If we define the number of components in the above way restrictions to the phase rule have been established. It has been sought to reduce the exceptions to the phase rule through a suitable definition; however, these experiments have not succeeded. (*Lehrbuch der Thermodynamik* van der Waals and Kohnstamm II, 506, Leipzig (1912).) The method adopted by Roozeboom of general and concrete definition of the components even if leading to the previously discussed restrictions to the phase rule is in any case the clearest and most welcome to the student.

INDEX OF METAL PAIRS WHOSE EQUILIBRIUM DIAGRAM IS KNOWN

M. = Metallurgie.

Z. A. = Zeitschrift für anorgan. Chemie.

Z. P. = Zeitschrift für physikal. Chemie.

I. CONTINUOUS SERIES OF SOLID SOLUTIONS.

1. The Melting Curve has Neither a Maximum nor a Minimum.

Ag-Au	Raydt, Z. A. 78, 58.
Ag-Pd	Ruer, Z. A. 51, 315.
Au-Mn	Hahn und Kyropoulos, Z. A. 95, 105.
Au-Pd	Ruer, Z. A. 51, 391.
Au-Pt	Doerinckel, Z. A. 54, 333.
Bi-Sb	Hüttner und Tammann, Z. A. 44, 131.
Co-Fe	Ruer, Ferrum 11, 33.

Co-Ni	Guertler und Tammann, Z. A. 42, 353 und Ruer, Ferrum 10, 257.
Cu-Ni	Guertler und Tammann, Z. A. 52, 25.
Cu-Pd	Ruer, Z. A. 51, 223.
Cu-Pt	Doerinckel, Z. A. 54, 333.
Fe-Mn	Levin und Tammann, Z. A. 47, 136 und Rümelin, Ferrum 1915, 41.
In-Pb	Kurnakow und Pushin, Z. A. 52, 444.

2. The Melting-point Curve has a Minimum.

	Minimum at	
Au-Cu	883°	Kurnakow, Z. A. 54, 149.
Cu-Cr	1318°	Lewkonja, Z. A. 59, 293.
Cu-Mn	870°	Sahmen, Z. A. 57, 1.
Fe-Ni		Guertler und Tammann, Z. A. 45, 205.
		Ruer, M. 7, 415.
Fe-Pt	1500°	Isaac und Tammann, Z. A. 55, 63.
Fe-V	1380°	Vogel und Tammann, Z. A. 58, 73.
Mn-Ni	1030°	Žemčužny, Z. A. 57, 253.
Mn-Co	1162°	Hiege, Z. A. 83, 253.
Ni-V	1360°	Giebelhausen, Z. A. 91, 251.

II. SOLID SOLUTION SERIES WITH A SMALL GAP.

	Gap.	
Au-Fe	1168°: 37—72 Fe	Isaac und Tammann, Z. A. 53, 281.
	20°: 20—82 Fe	
Cd-Hg	190°: 75—77 Cd	Bijl, Z. P. 41, 641.
Cr-Ni	1300°	Voss, Z. A. 57, 34.
	Kleine Lücke bei	
	40 Ni	
In-Tl	180°: 30—37 In	Kurnakow, Z. A. 52, 430.
Mn-Zn		Siebe, Z. A. 108, 171.
Pb-Tl	180°: 6—23 Pb	Lewkonja, Z. A. 52, 452.

III. VERY LIMITED MISCIBILITY IN THE SOLID STATE.

	Eutectic Temperature	
Co-Cu	1107°: 5—90 Co	Sahmen, Z. A. 57, 1.
Cu-Fe	1100°: 3—97 Fe	Sahmen, Z. A. 57, 1, Ruer, Ferrum 10, 39.
Ag-Be	878°	Oesterheld, Z. A. 97, 1.
Ag-Bi	262°	Petrenko, Z. A. 50, 133.
Ag-Cu	778°	Lepkowski, Z. A. 59, 285.
Ag-Na	95°	Quercigh, Z. A. 68, 301.
Ag-Pb	305°	Petrenko, Z. A. 53, 202.
Ag-Si	800°	Arrivaut, Z. A. 60, 436.
Ag-Tl	287°	Petrenko, Z. A. 50, 133.
Al-Be	644°	Oesterheld, Z. A. 97, 1.
Al-Si	577°	Fränkel, Z. A. 58, 154.
Al-Sn	232°	Gwyer, Z. A. 49, 311.
Au-Bi	240°	Vogel, Z. A. 50, 145.
Au-Co	997°	Wahl, Z. A. 66, 60.
Au-Ni	950°	Levin, Z. A. 45, 238.
Au-Si	370°	Clara di Capua, Gazz. chim. ital. 50, I, 207.
Au-Tl	132°	Levin, Z. A. 45, 31.
Bi-Cd	146°	Stoffel, Z. A. 53, 137.
Bi-Cu	268°	Jeriomini, Z. A. 55, 412.
Bi-Hg	—40°	Pushin, Z. A. 36, 201.

Eutectic Temperature		
Bi-Pb	125°	Stoffel, Z. A. 53, 137.
Bi-Sn	137°	Stoffel, Z. A. 53, 148.
Cd-Pb	249°	Stoffel, Z. A. 53, 137.
Cd-Sn	177°	Stoffel, Z. A. 53, 137.
Cd-Tl	203.5°	Kurnakow, Z. A. 30, 86.
Cd-Zn	270°	Hindrichs, Z. A. 55, 415.
Hg-Pb	-42°	Jänecke, Z. P. 60, 399.
Hg-Sn	-39°	Heteren, Z. A. 42, 129.
Hg-Zn	-42.5°	Pushin, Z. A. 36, 201.
Pb-Sb	228°	Gontermann, Z. A. 55, 419.
Pb-Sn	180°	Degens, Z. A. 63, 212.
Sb-Si		Williams, Z. A. 55, 1.
Si-Sn	232°	Tamaru, Z. A. 61, 40.
Sn-Tl	170°	Kurnakow, Z. A. 30, 86.
Sn-Zn	204°	Rudberg, Pogg. Ann. 18, 240, 1830.

IV. ONLY SLIGHTLY MISCIBLE IN THE LIQUID STATE.

Ag-Co	Petrenko, Z. A. 53, 212.
Ag-Cr	Hindrichs, Z. A. 59, 414.
Ag-Fe	Petrenko, Z. A. 53, 212.
Ag-Mn	Arrivaut, Z. A. 83, 193.
Ag-Ni	Petrenko, Z. A. 53, 212.
Al-Bi	Gwyer, Z. A. 49, 311.
Al-Cd	Gwyer, Z. A. 57, 113.
Al-K	Smith, Z. A. 56, 109.
Al-Na	Mathewson, Z. A. 48, 191.
Ag-Pb	Gwyer, Z. A. 57, 113.
Al-Tl	Doerinkel, Z. A. 48, 185.
As-Bi	Friedrich, M. 5, 158.
Bi-Co	Lewkonja, Z. A. 59, 293.
Bi-Cr	Williams, Z. A. 55, 1.
Bi-Fe	Isaac und Tammann, Z. A. 55, 58.
Bi-Si	Williams, Z. A. 55, 1.
Bi-Zn	Spring, Z. A. 13, 29.
Ca-Fe	Quasebart, M. 3, 28.
Cd-Cr	Hindrichs, Z. A. 59, 414.
Cd-Fe	Isaac und Tammann, Z. A. 55, 58.
Co-Pb	Lewkonja, Z. A. 59, 293.
Co-Tl	Lewkonja, Z. A. 59, 293.
Cr-Cu	Hindrichs, Z. A. 59, 414.
Cr-Pb	Hindrichs, Z. A. 59, 414.
Cr-Sn	Hindrichs, Z. A. 59, 414.
Cr-Zn	Hindrichs, Z. A. 59, 414.
Cu-Pb	Friedrich und Leroux, M. 4, 299.
Cu-Tl	Doerinkel, Z. A. 48, 185.
Cu-V	Giebelhausen, Z. A. 91, 251.
Fe-Pb	Isaac und Tammann, Z. A. 55, 58.
K-Mg	Smith, Z. A. 56, 109.
Mg-Na	Mathewson, Z. A. 48, 191.
Mn-Pb	Williams, Z. A. 55, 1.
Ni-Pb	Voss, Z. A. 57, 34.
Ni-Tl	Voss, Z. A. 57, 34.
Pb-Si	Tamaru, Z. A. 61, 40.
Pb-Zn	Spring, Z. A. 13, 29.
Si-Tl	Tamaru, Z. A. 61, 40.
Tl-Zn	v. Vegesack, Z. A. 52, 30.

V. ALLOYS FORMING ONLY ONE COMPOUND.

	Formula of the Compound	
Ag-Pt	Ag ₂ Pt (End member of solid solution series)	Doerinckel, Z. A. 54, 333.
Ag-Sb	Ag ₃ Sb	Petrenko, Z. A. 50, 133.
Ag-Sn	Ag ₃ Sn	Petrenko, Z. A. 53, 200.
Al-Fe	Al ₃ Fe	Gwyer, Z. A. 57, 113.
Al-Mg	Al ₃ Mg ₂ (End member of solid solution series)	Grube, Z. A. 45, 225.
Al-Sb	AlSb	Tammann, Z. A. 48, 53.
Al-Zn	Al ₂ Zn ₃	Rosenhain und Archbutt, Philos. Transact. 211, A. 315.
Au-Na	Au ₂ Na	Mathewson, Int. Z. f. Metallogr. 1, 81.
Au-Sb	AuSb ₂	Vogel, Z. A. 50, 145.
Au-Te	AuTe ₂	Pellini und Quercigh, Atti ac. Linc. V, 19, 445.
Bi-Mg	Bi ₂ Mg ₃	Grube, Z. A. 49, 72.
Ca-Mg	Ca ₂ Mg ₃	Baar, Z. A. 70, 352.
Cd-Mg	CdMg	Grube, Z. A. 49, 72.
Cd-Te	CdTe	Kobayashi, Z. A. 69, 1.
Hg-Te	HgTe	Pellini, Atti ac. Linc. V, 18, 211.
Hg-Tl	Hg ₂ Tl ₃	Roos, Z. A. 94, 358.
K-Na	KNa ₂	Kurnakow, Z. A. 30, 109.
Mg-Pb	Mg ₂ Pb	Grube, Z. A. 44, 117.
Mg-Sb	Mg ₃ Sb ₂	Grube, Z. A. 49, 72.
Mg-Si	Mg ₂ Si	Vogel, Z. A. 61, 46.
Mg-Sn	Mg ₂ Sn	Grube, Z. A. 46, 76.
Mg-Zn	MgZn ₂	Grube, Z. A. 49, 72.
Pb-Te	PbTe	Fay, Journ. am. chem. soc. 27, 81.
Pb-Tl	PbTl ₃	Lewkonja, Z. A. 52, 452.
Sb-Te	Sb ₂ Te ₃	Fay, Journ. am. chem. soc. 27, 95.
Sb-Tl	SbTl ₃ ?	Williams, Z. A. 50, 127.
Sn-Te	SnTe	Fay, Journ. am. chem. soc. 29, 1265.
Te-Zn	TeZn	Kobayashi, Int. Z. f. Metallogr. 2, 65.

VI. ALLOY SERIES WITH SEVERAL COMPOUNDS OR SEVERAL MISCIBILITY GAPS.

Ag-Al	Petrenko, Z. A. 46, 49.
Ag-As	Heike und Leroux, Z. A. 92, 119.
Ag-Ca	Baar, Z. A. 70, 352.
Ag-Cd	Petrenko, Z. A. 70, 157.
Ag-Mg	Żemczużny, Z. A. 49, 400.
Ag-Te	Pellini und Quercigh, Atti ac. Linc. V, 19, 415.
Ag-Zn	Petrenko, Z. A. 48, 347.
Al-Au	Heycock und Neville, Philos. Transact. 194 A. 201.
Al-Ca	Donski, Z. A. 57, 185.
Al-Ce	Vogel, Z. A. 75, 41.
Al-Co	Gwyer, Z. A. 57, 136.
Al-Cr	Hindrichs, Z. A. 59, 414.
Al-Cu	Gwyer, Z. A. 57, 113.
Al-Mn	Hindrichs, Z. A. 59, 414.
Al-Ni	Gwyer, Z. A. 57, 113.
As-Cu	Friedrich, M. 5, 529.
Au-Cd	Vogel, Z. A. 48, 333.

Au-Mg	Vogel, Z. A. 63, 169 und 67, 442.
Au-Pb	Vogel, Z. A. 45, 11.
Au-Sn	Vogel, Z. A. 46, 60.
Au-Zn	Vogel, Z. A. 48, 319.
Bi-Ce	Vogel, Z. A. 84, 323.
Bi-K	Smith, Z. A. 56, 109.
Bi-Mn	Siebe, Z. A. 108, 171.
Bi-Na	Mathewson, Z. A. 50, 171.
Bi-Ni	Voss, Z. A. 57, 34.
Bi-Tl	Chikashigé, Z. A. 51, 328.
Ca-Cd	Donski, Z. A. 57, 185.
Ca-Cu	Baar, Z. A. 70, 352.
Ca-Pb	Baar, Z. A. 70, 352.
Ca-Tl	Baar, Z. A. 70, 352.
Ca-Zn	Donski, Z. A. 57, 185.
Ce-Fe	Vogel, Z. A. 99, 26.
Cd-Cu	Sahmen, Z. A. 49, 301.
Cd-K	Smith, Z. A. 56, 109.
Cd-Li	Masing und Tammann, Z. A. 67, 183.
Cd-Na	Mathewson, Z. A. 50, 171.
Cd-Sb	Treitschke, Z. A. 50, 217.
Ce-Cu	Hanamann, Habilitationsschrift, Boroträger Leipzig 1915.
Ce-Fe	Vogel, Z. A. 99, 26.
Ce-Mg	Vogel, Z. A. 91, 277.
Ce-Sn	Vogel, Z. A. 72, 319.
Co-Sb	Lewkonja, Z. A. 59, 293.
Co-Si	Lewkonja, Z. A. 59, 293.
Co-Sn	Lewkonja, Z. A. 59, 293.
Cr-Sb	Williams, Z. A. 55, 1.
Cs-Hg	Kurnakow, Z. A. 52, 416.
Cu-Mg	Sahmen, Z. A. 57, 1.
Cu-Sb	Baikow, Journ. russ. phys.-chem. Ges. 36, III.
Ci-Si	Rudolfi, Z. A. 53, 216.
Cu-Sn	Heycock und Neville, Philos. Transact. 202 A, 1.
Cu-Te	Chikashigé, Z. A. 54, 50.
Cu-Zn	Tafel, M. 5, 343.
Fe-Sb	Kurnakow, Z. A. 58, 1.
Fe-Si	Guertler und Tammann, Z. A. 47, 163.
Fe-Sn	Isaac und Tammann, Z. A. 53, 281.
Hg-K	Jänecke, Z. P. 53, 245.
Hg-Na	Schüller, Z. A. 40, 385.
Hg-Rb	Kurnakow, Z. A. 52, 423.
K-Pb	Smith, Z. A. 56, 109.
K-Sn	Smith, Z. A. 56, 109.
K-Tl	Kurnakow, Z. A. 30, 86.
K-Zn	Smith, Z. A. 56, 109.
Li-Sn	Masing und Tammann, Z. A. 67, 183.
Mg-Ni	Voss, Z. A. 57, 34.
Mg-Tl	Grube, Z. A. 46, 76.
Mn-Sb	Williams, Z. A. 55, 1.
Mn-Si	Doerinckel, Z. A. 50, 117.
Mn-Sn	Williams, Z. A. 55, 1.
Na-Pb	Mathewson, Z. A. 50, 171.
Na-Sb	Mathewson, Z. A. 50, 171.
Na-Sn	Mathewson, Z. A. 50, 171.
Na-Te	Pellini und Quercigh, Atti ac. Linc. V, 19, 350.
Na-Tl	Kurnakow, Z. A. 30, 86.
Na-Zn	Mathewson, Z. A. 48, 191.
Ni-Sb	Lossew, Z. A. 49, 58.

Ni-Si	Guertler und Tammann, Z. A. 49, 93.
Ni-Sn	Voss, Z. A. 57, 34.
Ni-Zn	Tafel, M. 5, 413.
Pb-Pd	Ruer, Z. A. 52, 345.
Pb-Pt	Doerinckel, Z. A. 54, 333.
Pd-Sb	Sander, Z. A. 75, 97.
Pt-Sb	Friedrich und Leroux, M. 6, 1.
Pt-Sn	Doerinckel, Z. A. 54, 333.
Sb-Sn	Williams, Z. A. 55, 1.
Sb-Zn	Žemčužny, Z. A. 49, 384.

VII. INCOMPLETELY INVESTIGATED SYSTEMS.

Ag-As	Friedrich und Leroux, M. 3, 192.
Ag-Hg	Reinders, Z. P. 54, 622.
Ag-Se	Friedrich, M. 5, 355.
As-Au	Schleicher, I. Z. f. M. 6, 18.
As-Co	Friedrich, M. 5, 150.
As-Fe	Friedrich, M. 4, 129.
As-Hg	Dumesnil, Compt. rend. 152, 868.
As-Mn	Schoen, M. 8, 739.
As-Ni	Friedrich und Bennigson, M. 4, 200.
As-Pb	Friedrich, M. 3, 41.
As-Pt	Friedrich und Leroux, M. 5, 148.
As-Sn	Parravano, Atti ac. Linc. 20, 593.
As-Zn	Friedrich und Leroux, M. 3, 477.
Au-Al	Heycock und Neville, Proc. Roy. Soc. Lond. A 90, 560.
Au-Hg	Parravano, Gazz. chim. 48, II, 123.
B-Fe	Hannesen, Z. A. 89, 257.
B-Ni	Giebelhausen, Z. A. 91, 251.
Be-Cu	Oesterheld, Z. A. 97, 1.
Be-Fe	Oesterheld, Z. A. 97, 1.
Bi-Ca	Donski, Z. A. 57, 185.
Bi-Mn	Siebe, Z. A. 108, 171.
C-W	Ruff, Z. A. 85, 292.
Ca-Sn	Donski, Z. A. 57, 185.
Ca-Sb	Donski, Z. A. 57, 185.
Ca-Si	Tamaru, Z. A. 62, 81.
Cd-Ni	Voss, Z. A. 57, 34.
Ce-Pb	Vogel, Z. A. 72, 319.
Co-P	Žemčužny, Z. A. 64, 245.
Co-Zn	Lewkonja, Z. A. 59, 293.
Cr-Fe	Treitschke und Tammann, 55, 402.
Cu-P	Heyn und Bauer, Z. A. 52, 129.
Fe-Mo	Lautsch und Tammann, Z. A. 55, 386.
Fe-P	Konstantinow, Z. A. 66, 209.
Fe-Ti	Lamort, Ferrum 11, 225.
Fe-W	Honda, Science Rep. Tohoku Imp. Univ. VI. 5, 236.
Fe-Zn	v. Vegesack, Z. A. 52, 30.
Mn-P	Žemčužny, Journ. russ. Phys.-chem. Ges. 39, 777.
Ni-P	Konstantinow, Z. A. 60, 405.
Pt-Tl	Hackspill, Compt rend. 146, 820.
Si-V	Giebelhausen, Z. A. 91, 251.

VIII. TERNARY AND QUATERNARY SYSTEMS, See p. 369.

1641

SUBJECT INDEX.

A

- Affinity Constants
of metallic compounds, 223
- Alloys
 - Chemical and electrochemical prop-
erties, 305
 - Color of, 279
 - Conductivity, 293
 - Crystallization, 353
 - Heusler, 289
 - Influence of temperature on conduc-
tivity, 298
 - Low melting, 369
 - Parting of, 313
 - Physical properties of, 271
 - Potential of, 333
 - Solubility of Hydrogen in, 309
 - Ternary, Alloys of
 - Aluminum, 370
 - Copper, 370
 - Iron, 371
 - Magnesium, 370
 - Silver, 369
 - Aluminum, Ternary alloys, 370
- Amorphous masses, 21
 - theory, 66
- Analysis, thermal, 176
- Anisotropy, 19
- Annealing, 248
- Antimony, 15

B

- Beryllium, Aluminum, system, 30
 - Silver, system, 30
- Beta, Iron, 25
 - diffusion of carbon in, 214
- Bismuth, 15
 - nucleus formation in, 27
 - single crystals of, 26
- Binary, Physical properties of, alloys, 271
 - Magnetic properties of, alloys, 281
 - Mixtures, relation of metals in, 214
 - surfaces of heat, content of, 164
- Systems, 147
 - Equilibrium diagrams of, 234
 - Relation between structure and
thermal phenomena, 182

- Boiling points of metals, 35
- Brinell hardness, 292

C

- Cadmium, 17
 - Interstitial substances in, 17, 18
- Camazite, 257
- Carbon, 25
 - Iron system, 234
- Cathodic, polarization, 345
 - precipitation, 330
- Chemical compounds, 222
 - properties of alloys, 305
 - reactivity limits, 140
- Chloroform, solubility in water, 64
- Cold work, influence on color of al-
loys, 140
 - Influence on ferro-magnetic proper-
ties, 144
 - metals, strains in, 91
- Color, of alloys, 140, 279
- Composition, specific volume, 271
- Compounds, ability of elements to
form, 228
 - Decomposition on melting, 153
 - Formation, 197
 - Heat of formation, 278
 - Malleability of, 73
 - Melting to a homogeneous liquid, 152
 - Potential concentration, 342
 - Separating into two layers on melt-
ing, 157
 - Specific heat of, 278
 - Valence of metals in their, 230
- Compressed powders, 205
- Conchoidal fracture, 76
- Conductivity
 - Electrical, of alloys, 293
 - Heat, 303
 - and hardness, 301
 - Influence of temperature, 298
 - of liquid mixtures, 300
- Conglomerates, 205
 - Changes of, 273
- Cooling
 - Transformation of austenite into
martensite by, 251
 - Effect of rapid, 245
 - Curves, 42

- Copper, 16, 370
 - Bismuth, system, 29
 - Gold, parting, 313
 - Gold alloys, 305
 - Gold, system, 266
 - Nickel, 264, 308
 - Palladium, 308
 - Silver, 265
 - Tin, 259
 - Zinc, 262
 - Copper, Crystallization out of Cu-Bi melts, 30
 - Structure of cast, 16
 - Cored structure, 185
 - Critical point, 34
 - Crompton, Law of, 40
 - Crystal, Size, 26
 - Form of, 29
 - Rounded, 30
 - Preparation of, 26
 - Single, 26
 - Crystallites, 15
 - Crystallization, Anomalies in solid solutions, 185
 - Eutectic, 182
 - of iron-carbon melts, 235
 - in ternary systems, 353
 - of solid solutions, 363
 - Spontaneous, 18
 - Summary of, 368
 - Velocity, 18, 22
- D
- Deformation, Homogeneous, 67
 - Permanent, 76
 - Dendrites, 15
 - Density, Change on working, 125
 - Diffusion, 211
 - by polarization, 345
 - Dilatation, Thermal, 275
 - Dissociation, in anisotropic state, 191
 - Dulong and Petit, Law of, 40
- E
- Elastic limit, 78, 80
 - Elastic properties, recurrence of, 110
 - Electrical, conductivity, 47
 - of liquid metals, 48
 - change on working, 66
 - change on wire drawing, 130
 - Electrochemical, properties of alloys, 305
 - Electrolytes, reaction of metals with, 61
 - Electrolytically precipitated metals, 136
 - Electrolytic conductivity, 50
- Electromotive, force of a transition cell, 64
 - series, 61
 - Elementary crystal, 19
 - Equilibrium diagram, 34, 149
 - of special binary systems, 234
 - Equilibrium, Theory, 333
 - Etching pits, 16
 - Eutectic, crystallization, 182
 - structure, 183, 184
 - Extrusion rate, 113
 - of metals, 117
- F
- Ferromagnetic metals, transition points, 38
 - properties, 144
 - Ferromagnetism, 246, 281
 - loss in nickel, 264
 - Fibrous structure, 66
 - Flow of metal conglomerates, 71
 - Flow of metals, 78
 - Flow pressure, solid solutions, 290
 - Formation, heat of, 278
 - Fusion, heat of, 278
 - Fracture, conchoidal, 76
- G
- Gases, solubility of, in metals, 54
 - Glass formation, 18
 - Glide lines, 68
 - Glide planes, 16
 - Glide surfaces, influence on rate of solution, 138
 - Gold-Silver system, 266
 - Gold, surface tension, 28
 - Grain growth, 13
 - Grain size, 96
 - Granular structure, 31
- H
- Hardness, 82
 - absolute, 83
 - Brinell, 84
 - and conductivity, 301
 - solid solutions, 290
 - Hardening above flow limit, 89
 - Heat conductivity, 303
 - Heat content, 40
 - change during softening, 19
 - surfaces of, 164
 - Heat, extraction of, 250
 - Heat of formation, 278
 - Heat of fusion, 43, 278
 - Heat of transition, 43, 65
 - Heusler, alloys, 289
 - Hydrogen, solubility in alloys, 309

I

- Ice, extrusion velocity, 113
- Interference pattern, 76
- Interstitial substance, 17
- Ions, occurrence of, 345
- Iron, 16, 371
 - carbon system, 234
 - chromium alloys, 123
 - forms of, 250
 - microstructure, 17
 - nickel system, 255
 - penetration of carbon into, 213
 - silicon, system, 253
 - alloys, 307
 - tempering of, 58
 - vanadium alloys, 308
- Isomorphism of elements, 231

L

- Law of Wiedemann and Franz, 303
- Lead-Tin system, 267
- Lever relation, 149
- Linear crystallization velocity, 18, 22
- Liquids, immiscible, 156
- Liquid air, transformation of austenite into martensite by cooling in, 251
- Load-elongation curves, 85, 86
- Low melting, ternary alloys, 369

M

- Magnesium, 370
 - Aluminum system, 268
 - silver alloys, 308
- Magnetic properties of metals, 51
 - of binary alloys, 281
 - of Heusler alloys, 289
- Magnetite, 50
- Malleability, 72
- Manganesc, 25
- Maximum, melting point, 36, 161
- Mechanical properties, effect of temperature on, 120
- Melting, 20
 - by pressure, increases, 116
 - curve, 34
 - curves of metals, 118
 - properties that do not change on, 62
 - transient, 112
 - volume change on, 45
- Melting point, 62
 - electrical conductivity at, 48
 - maximum, 36
- Metallic compounds, affinity constants of, 233
- Meteoritic, nickel-iron, 257
- Microscopic investigation, 187

- Microscopic method for elastic limit, 80
- Minimum melting point, 161
- Miscibility, complete, 157
 - limited, liquid state, 265
- Modification, hypothesis, 66
- Modulus of elasticity, 119
 - change on working, 65

N

- Nernsts' theorem, 40
- Neumann lines, 139
- Neumann-Kopp, law of, 41
- Neutral curve, 36
- Nickel-iron, meteoric, 257
- Nitric acid, in parting of alloys, 313
- Nuclei number, 19, 24

O

- Occluded gas, evolution on recrystallization, 105
- Osmotic pressure, 63
- Oxide, electrical conductivity, 50

P

- Palladium, solubility of hydrogen in, 309
- Paramagnetism, 287
- Parting, of alloys, 313
- Phase Rule, 372
- Pipe formation in ingots, 46, 47
- Plasticity, 70
- Plessite, 257
- Polarization, steels, 347
- Polymorphic, transformation reactions caused by, 195
- Potential, of alloys, 333
 - of metals, 61
 - concentration in compounds, 342
 - concentration in solid solutions, 336
- Precipitation, of alloys, 332
- Pressure, conglomerates, 273
 - flow, solid solutions, 290
 - influence of, on transformation temperatures, 251
 - of maximum melting point, 36
 - slip lines, 292
- Properties, chemical and electrochemical of alloys, 305
 - physical, of binary alloys, 271

R

- Rate of solution, 138
- Reactions, in solid state, 190
 - caused by polymorphic transformations, 195

- Reaction limits, explanation of, 323
 relation to space lattice, 314
 solid solutions, 305, 326
 space lattice, 324
- Recrystallization, 15, 93
 diagram, 101
 rate, 99
 temperature, 100, 108
 velocity, 110
- Resistance, decrease on heating, 135
 of ternary alloys, 302
- Rupture, path of, 16
- S
- Silver, alloys, 369
 -gold, alloys, 305
 -gold, parting of, 313
 surface tension of sheet, 28
- Simple displacement, 68
- Slip lines, 292
- Softening interval, 19
- Solid solution, crystallization in ternary mixtures, 363
 hardness and flow pressure, 290
 potential concentration, 336
- Solid solutions, reaction limits, 305, 326
 series with gaps, 162
 series without maximum or minimum melting point, 159
- Solid state, reactions in, 190
- Solution, velocity, 62
- Solubility, of base metals, 342
 gap, rule regarding position of, 231
 of hydrogen in alloys, 309
- Space canals, formation of, 124
- Space lattice, isomerism, 329
 of metals, 32
 changed by permanent deformation, 76
 normal distribution, 318
 reaction limits, 324
 regular distribution of atoms, 316
 relation to reaction limits, 314
- Specific heat of metallic compounds, 276
- Specific volume, 44, 271
- Spherulites, 15, 16
- Stainless steels, 347
- Steels, high speed, 257
 stainless, 347
 ternary carbon, 256
 transformations in carbon-, 239
- Strain, action on crystal in contact with melt, 112
- Strains in cold worked metals, 91
- Sulfides, electrical conductivity, 50
- Supercool, tendency to, 24
- Supercooled, liquid vapor pressure of, 63
- Supercooling, 23
- Superconductors, 49
- Surface, of crystallization of a ternary compound, 362
 tension of solid bodies, 28
- Susceptibility, magnetic, 51
- Systems, equilibrium diagrams of special binary, 234
 copper-bismuth, 29
 copper-gold, 266
 copper-nickel, 264
 copper-silver, 265
 copper-tin, 257
 copper-zinc, 262
 gold-silver, 266
 iron-carbon, 234
 iron-chromium, 123
 iron-nickel, 255
 iron-silicon, 253
 lead-tin, 267
 magnesium-aluminum, 268
 tin-antimony, 269
- T
- Taenite, 257
- Temper colors, 56
- Temperature, conglomerates, 273
 coefficient of extrusion, rate, 115
 effect on mechanical properties, 120
 influence on conductivity, 298
 of minimum resistance, 134
 alloys, electrical resistance, 302
 carbon steels, 256
- Ternary, mixture, graphic representation, 351
 mixtures, crystallization of solid solutions, 363
 system, crystallization, 353
- Theory, equilibrium, 333
- Thermal, analysis, 176
 dilatation, 275
- Thermodynamic, potential, 64
- Thermoelements, 64
- Thermoelectric force of alloys, 304
- Thermal investigations, 189
 phenomena, in binary systems, 182
- Thermoelectric force, 142
- Three component systems, 351
- Tin-antimony system, 269
- Transformation, influence of pressure, 251
 in carbon steels, 239
 of austenite into martensite, 251
- Transition, cell, 64
 heat, 43, 65
 points, 37

- points, electrical conductivity at, 50
- magnetic changes, 54
- Transient melting, 112
- Translation, 67
- Twinning, 102
 - lamella, 71
- V
- Valence, of metals in their compounds,
 - 230
- Vapor pressure, 62
- Viscosity, 20
- Volume change produced by deformation, 18
- Volume change on melting, 45
- Volume, changes of conglomerates, 273
- Volume specific, 271
- W
- Wiedemann and France, law of, 303
- Working, of amorphous-masses, 21
- Working metals, 65
- Z
- Zinc, 15

AUTHOR INDEX.

A

Adams, 127
Addicks, 131
Alexejew, 156, 157
Andrew and Edwards, 371
Arnold and McWilliam, 259
Auerbach, 83, 84

B

Bach, 85
Backstrom, 130
Baedeker, 47
Bancroft, 375
Barlow, 369
Barret, Brown and Hadfield, 297
Barus, 34, 45, 298
Bauer and Arndt, 186
Bauschinger, 89
Beilby, 66, 127
Bekier, 27
Belajew, 259
Benedicks, 250, 257, 294
Bergman, 135, 137
Berry, 223, 310
Berwerth, 257
Berwerth and Tammann, 257
Beurath, 302
Bijl, 336
Biltz and Hohorat, 278
Block, 26, 44
Bohlin, 32
Borelius, 143, 304, 349
Bornemann, 11, 13, 157, 216, 259, 262, 300
Bose, 50
Bragg, 32, 323
Bredig, 64
Bridgman, 87, 118
Bruni, Sandonnini and Quercigh, 376

C

Carpenter and Elam, 106
Ceccarelli, 369
Cesaris, 371
Chappel and Levin, 129
Charpy, 235, 238, 369
Chikashige, 280
Cohen, E., 39, 64, 136, 332
Cohn, P., 132

Credner, 108, 132, 133, 135, 136
Czoehralski, 101, 104, 120

D

Dahl and Tammann, 73
Davey, 138
Debye, 32
Debye and Scherrer, 77
Dewar and Fleming, 298
Doelter, 21, 31
Dulong, 44

E

Endell and Hanemann, 189
Ericson-Auren, 62
Ewig, 245

F

Faust, 95, 136
Faust and Tammann, 69, 80, 82, 127
Ferche, 63
Fischbeck, 303
Fraenkel, 67, 370
Fraenkel and Heuten, 212
Fraenkel and Tammann, 257
Friedrich and Leroux, 265, 370
Fuchs, 164, 342

G

Gallagher, 670
Geibel, 302, 304, 349
Gewecke, 131
Giolitti, 371
Giolitti and Tavante, 259
Gibbs, 148
Goebel, 369
Goerens, 95, 111, 112, 119, 126, 139, 145, 371
Goerens and Ellinger, 31
Goerens and Ruer, 13, 189
Gontermann, 240, 371
Grube, 198, 268, 297
Guertler, 294, 296
Guertler and Tammann, 193, 199, 203, 253, 264
Guillaume, 275
Guillet, 256, 292, 371

Gutowsky, 239
Gwyer, 195

H

Haken, 305
Hanemann, 235, 248
Harrison, 50
Hartel, 122
Herschkowitz, 342
Herz, 83, 84
Heusler and Richarz, 289
Heycock and Neville, 259, 265
Heyn, 91, 93, 94, 100, 136, 140, 235, 248
Heyn and Bauer, 91, 139
Hindricks, 164, 289
Hollmann, L., 349, 375
Hollmann, R., 166, 175
Honda, 52, 53, 287, 289
Honda and Takagi, 244
Hort, 128
Huijet, 370
Hull, 33
Hunter and Bacon, 303

I

Isaac, E., and Tammann, 194, 198

J

Jänecke, 266, 363, 369, 370
Jandler and Tammann, 223
Johnston, 127
Johnston and Adams, 118
Juhlin, 63

K

Kahlbaum, 125, 126, 127
Kick, 72
Koenigsberger, 39, 50, 189
Kohlrausch, 50
Konstatinow and Smirnow, 270
Kopp, 165
Körber, 37, 89, 90
Körber and Wieland, 82
Köster and Tammann, 57
Kreman, 344
Kroll and Ewen, 106
Kuhny and Augsburg, 141
Kurnakow, 294
Kurnakow and Puschin, 290
Kurnakow, Puschin and Senkowsky, 302
Kurnakow and Smirnow, 290, 295, 301
Kurnakow and Urasow, 253
Kurnakow and Žemežušny, 192, 266, 290, 292

L

Laue, 32
Landolt, 13
Le Chatelier, 50, 235, 293
Le Chatelier and Robin, 103
Lepkowski, 265
Levi-Malvano, 369, 371
Levin, 242
Levin and Meuthen, 244
Levin and Schottky, 130
Lewkojeff and Tammann, 117
Lewkonja, 204, 289
Liebisch, 142
Lindeck, 265
Lisell, 49
Loebe, 369
Lorenz, 50
Lorenz and Plumbridge, 369
Lossew, 201
Lownds, 143
Ludwick, 119, 123

M

Maey, 272
Mars, 256
Martens, 93, 121, 122
Martens and Heyn, 91
Masing, 101, 207
Matthiesen, 293
Matthiesen and Bose, 133
Matteucci, 130
Maurer, 246, 251
McKeehan, 33
Mendeleejew, 228
Meyer and Wogen, 212
Moellendorf and Czoehralski, 87
Morris, 50
Mügge, 67, 69, 126
Muller, 24
Murakami, 253
Mylius and Fromm, 332

N

Nernst, 333
Neumann, 138
Neumann-Kopp, 44, 221
Noll, 143
Nowack, 308, 312

O

Oberhoffer, 101
Oesterheld, 30
Onnes, 49
Osmond, 50, 106, 234, 240, 257
Osmond and Werth, 139

P

Palmaer, 62
Parravano, 370, 371

Parravano and Viviani, 370
 Parravano and Sirovich, 369
 Petit, 44
 Petrenko, 193
 Pionchon and Hill, 286
 Polanyi, 90
 Portevin, 98, 371
 Puschin, 340
 Puschin and Laschtschenko, 343
 Putz, 371

R

Rassow and Velde, 101
 Raydt, 266
 Reinders, 333, 336
 Reusch, 68
 Rinne, 76
 Roberts-Austen, 212, 234, 253, 262
 Robin, 98
 Roos, 279
 Roozeboom, 148, 172, 191, 196, 235, 351
 Roozeboom and Hoitsema, 309
 Rose, 124
 Rosenhain and Humfrey, 122
 Rosenhain and Tucker, 268
 Rudeloff, 120
 Rudolfi, 304
 Ruer, 13, 189, 235, 344
 Ruer and Goerens, 240
 Ruer and Iljin, 239
 Ruer and Klesper, 240
 Runge, 212

S

Sahmen and Von Vegesack, 356
 Salmen, 365
 Saner, 199
 Sauerwald, 108, 331, 340
 Schaller, 120
 Scherrer, 32, 136, 323
 Schilling, 39
 Schimpff, 277
 Schönert and Tammann, 212
 Schottky, 28, 128
 Schreinemakers, 351
 Schübel, 277
 Schultze, 303
 Schroder, 60
 Schwarz, 96
 Shepherd, 194, 262
 Shepherd and Blough, 259

Siehe, 308
 Sieverts, 54, 55, 310
 Smits, 66
 Sommerfeldt, 165
 Sotter and Tammann, 348
 Spring, 104, 127, 138, 205
 Spring and Romanoff, 157
 Stark, 75
 Stepanow, 296, 298
 Sturn, 125

T

Tafel, 262, 371
 Tammann, 19, 80, 291, 292
 Tammann and Mausuri, 107
 Tammann and Wiederholt, 345
 Terwoght, 228
 Thiel, 102
 Thoma, 310
 Thompson, 366
 Thomson, 142
 Thomson and Newhall, 146
 Thomson and Tait, 67
 Toepler, 46
 Tomlinson, 49
 Tschernow, 99

V

Van Alkemade, 148
 Van Eyk, 196
 Van't Hoff, 64, 286
 Vegard, 32, 323
 Vogel, 106, 183, 230, 269, 273, 363, 370, 371
 Vogel and Tammann, 371
 Voigt, 142
 Von Vegesack, 360, 370
 Von Wartenberg, 223
 Voss, 201

W

Wachlert, 371
 Wartenberg, 120
 Weber, 288
 Werner, 39, 51, 286
 Wertheim, 118
 Wever, 90
 Williams, 200, 269
 Wittorff, 235
 Wologdin, 292
 Wright, 366
 Wust and Goerens, 371